To Felicia M. Bush (Cook)

You will be missed.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Howard S. Weinberg, for his patience and guidance throughout my time at UNC. I would also like to thank Philip C. Singer for not only being a reader but also a co-principal investigator for this project. Special thanks must be given to Michael D. Aitken for being a reader and an excellent teacher.

My heartfelt gratitude must be given out to my friends at UNC for their support throughout all the challenging times – John, SuperKater, Kate, Owen, Matt, Zac, Eric, Dan, Sunny, Thom, Taku, Laura, Michael, Jill, Heather, and Fred. Also, without my friends for Syracuse not only supporting and encouraging me to attend graduate school but also their help during school, this report would have been impossible – John, Jon, Greg, Dave, Phil, Wendy, Bill, Alicia, Pavel, Scott, Tiff, Robin, and Sco. I would also like to thank my family for all their support during my studies here, without them this report would have never happened.

I need to thank the Water Resources Research Institute (WRRI) for funding this project. O.I. Analytical, your graciousness in loaning us the flow injection cyanide analyzer is most appreciated. Special thanks must be given out to William Frazier, Marti Groome, Kathy Southern, and Alan Isely for their help in all my sampling at the various wastewater treatment plants across North Carolina.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

bdl	Below Detection Limit
CN	Cyanide
DI	Deionized
FCN	Free Cyanide
FIA	Flow Injection Analysis
IC	Ion Chromatography
l	liter
µg	microgram
µl	microliter
mg	milligram
MDL	Minimum Detection Limit
NA	Not Available or Not Applicable
ppb	Part per Billion
ppm	Part per Million
PQL	Practical Quantification Limit
TCN	Total Cyanide
UV	Ultraviolet

CHAPTER I

INTRODUCTION

Cyanide is well known as a toxin to humans and aquatic life. Consequently, limits on the discharge of cyanide have been imposed to protect the environment. Concentrations as low as 5 ppb have been reported to be detrimental to sensitive aquatic life; thus, the strictest limits for cyanide discharge are placed on wastewater treatment plants. Measurements for cyanide in wastewater are not very consistent at this concentration, so any type of interference or contamination will influence a facility's ability to demonstrate compliance with its discharge permit.

This study formed part of a project conceived by a consortium of North Carolina wastewater utilities that continued to violate discharge permits for a variety of species. The study was designed to determine sources of any interference or contamination that could lead to a bias in cyanide measurements using existing methodology. An earlier component of the larger study indicated that those plants using chlorination were most likely to have recurrent problems meeting their discharge permit levels for cyanide. In addition, the analytical method for total cyanide as practiced at the utility or contract laboratories was found to suffer many shortcomings. Published literature states that both nitrite and sulfide are known to interfere with the total cyanide analysis. This research, therefore, aimed to study the potential artifactual presence of cyanide utilizing an alternative methodology.

The data collected from the various experiments were intended to validate if the cyanide formation was truly occurring in the chlorination process or if the cyanide were an artifact of the testing methodology. This was designed to be done through sampling before, during and after the chlorination process. These wastewater samples were then treated to identify where the cyanide formation reaction was occurring and the chemical species involved. Determination of the levels of these chemical constituent was also performed to observe any correlation exists between these species and effluent cyanide concentrations. These collected wastewater samples were treated in a variety of ways to account for possible chemical interferecces that may contribute to high cyanide concentrations. Approaches were then developed to control these reactions and to assure stabilization of collected samples during analysis.

This study attempts to furnish an approach for wastewater utilities to ensure accurate monitoring of total cyanide in their effluent, and thereby identify the source of true cyanide contamination when permit violations occur.

CHAPTER 2

LITERATURE REVIEW

2.1 CYANIDE CHEMISTRY BACKGROUND

Cyanide (CN^-) chemistry has been long studied for its toxic effects to humans and to the environment. Cyanide refers to all of the CN groups that can be determined as the cyanide ion, CN^- (APHA, 1995). Many different forms of cyanide exist including organic and inorganic (WHO, 1988). Four categories of cyanide are classified:

Free CN^-

Simple $A(CN)_x$

Complex $A_y[M(CN)_x]$

Organic $R-\underset{|}{C}-C\equiv N$

Simple cyanide refers to all the fractions of cyanide that exist as the free cyanide ion, CN^-, or the protonated form of the cyanide ion, hydrogen cyanide, HCN (Pohlandt et al., 1983). Simple cyanide is also called free cyanide. The acid disassociation constant, pK_a, for hydrogen cyanide is 9.21 at 25°C (CRC, 1995). Another property of free cyanide is pH dependence of the volatility. Hydrogen cyanide is highly volatile, but the cyanide ion is very soluble (Wild et. al, 1994). Therefore, at pH values well below the pK_a, such as the pH of typical natural waters and municipal wastewaters, the dominant form is hydrogen cyanide. High pH solutions will contain the cyanide ion form which is very soluble in water.

$$HCN(aq) + H_2O(l) = CN^-(aq) + H_3O^+(aq), \quad pK_a=9.21$$

Free cyanide can also be in a salt form. Such examples are sodium cyanide, NaCN, or potassium cyanide, KCN. These salts will dissociate in the presence of water to form the cyanide ion and the associated cation. The symbol "A" in the chemical equation below refers to a cation that is bound to the cyanide ion, and "x" is the number of cyanide groups attached to the cation.

$$A(CN)_x(s) \rightarrow xCN^-(aq) + A^{x+}(aq)$$

The cyanide molecule can also act as a ligand to bind with metals to form stable complexes (Pohlandt et al., 1983). The stability of these complexes depends on the type of metal and its

oxidation state (Cotton and Wilkinson, 1972). Metals that can become a part of this complex include cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), and iron (Fe) (Lordi et al., 1980). The Fe (III) complex is very stable thus rendering this compound virtually non-toxic, although the iron complexes can undergo photolytic decomposition (Doudoroff, 1976). The relationship between the complex species and the free species depends on the pH and metal concentrations.

Cyanide may exist as a part of an organic molecule. A triple bond between a carbon atom and a nitrogen atom in a larger organic compound is classified as organic cyanide, and the cyanide component may be released during degradation.

Analytical distinction of the different classifications of cyanide is difficult to perform. Because of this, cyanide concentrations are often reported in terms of total cyanide. This is the sum of free, simple, and complex cyanide (APHA, 1995). Total cyanide does not include organic cyanide.

The dominant cyanide species in municipal wastewater are the metal complexes. A study listing various domestic wastewater treatment plant raw wastewater cyanide speciation found that 74-83% of the total cyanide was of the complexed form (Lordi et al., 1980). The remaining fraction was of free form. This speciation is similar to that found in unpolluted natural waters (Sekerka and Lechner, 1976).

2.2 Toxic Effects of Cyanide

The toxicity of hydrogen cyanide is well known. The main cyanide species of concern for toxicity is hydrogen cyanide, HCN, (Wild 1994). Therefore, the basis of the cyanide discharge limits for wastewater treatment plants are based on the detrimental effects of hydrogen cyanide on aquatic life. Hydrogen cyanide concentrations as low as 10 μg/l as CN^- have been reported to kill some sensitive animal species in water (Blaha, 1976). Early assessment of aquatic life's response to cyanide was carried out on freshwater invertebrates that would have a response similar to freshwater fish. These invertebrates were *Asellus communia* and *Gammarus pseudolimnaeus* (USEPA, 1984). In addition, the ionic form of cyanide, CN^-, is of concern since it can act as a non-specific enzyme inhibitor. Specifically, this inhibition affects the cytochrome oxidase thus preventing the uptake of oxygen by living tissue (WHO, 1988). Early development stages, i.e. embryonic or early juvenile stages, of aquatic life are the most susceptible to cyanide poisoning (Billard and Roubaud, 1985). Toxicity of complex cyanide is associated with the

breakdown of the complexes into free cyanide and the associated metal (Wild et al., 1994). The toxicity is then from both the free cyanide and the metal, some of which can be extremely toxic. An example of this is cadmium or lead cyanide complex. These complexes are not as stable as other complexes, so decomposition is much more likely. The toxicity of the metals are generally considered to be less than the cyanide; however, there may be an additive effect (Blaha, 1976).

2.3 Discharge Limits

Determination of the cyanide discharge limits is founded on the toxicological findings. Each state is then allowed to raise or lower the limit with the provision that it can demonstrate that the revised limit will not have an adverse effect on the environment based on the receiving-water quality. This option is open to all utilities who feel the discharge limit was unfairly set, although demonstrated arguments must stand up to the scrutiny of the State regulatory agency.

The discharge permit requires that a grab sample for total cyanide analysis must be taken at least once a week at the effluent end of the plant. This sample can be analyzed by the utility or by an approved commercial laboratory. If more than one sample is taken in a week, the average of those samples is then reported to the State.

2.4 Cyanide Sources

Sources of cyanide to a municipal wastewater treatment plant can have three different origins: domestic discharges, atmospheric deposition/surface run-off, and commercial/industrial discharges. Domestic discharge can contribute a significant amount (up to 90%) of total wastewater flow to a wastewater treatment facility (Metcalf and Eddy, 1991). Cyanide may exist in natural organic material found in domestic sewage and could be released during biodegradation (WHO, 1988). However, it is believed that as a contribution to the cyanide content of raw sewage to the plant, this source of cyanide is quite small.

One possible source of cyanide from run-off origins could be from road salt that contains cyanide as an anti-sticking agent (Wild et al., 1994). There has not been extensive study on the quantification of cyanide attributed to run-off and atmospheric deposition. However, since cyanide concentrations in the atmosphere are very low (WHO, 1988) and at least in North Carolina road salt is rarely used, this is likely to be an insignificant source of cyanide.

With the previous two sources of cyanide believed to be small, cyanide detected in the influent should mostly be attributed to industrial/commercial applications of cyanide in the manufacturing processes. Examples of industries that have historically discharged elevated levels of cyanide are photographic development facilities, electroplating industries, case hardening plants, chemical plants, smelting operations, steel plants, coal-gasification industries, mining operations, and petroleum refining industries (Yoshida et al., 1983; Theis and West, 1986; Young and Theis, 1991; Meeussen et al., 1992). Cyanide concentrations can vary widely from industrial discharges. Values from 0.01 mg/l to 10 mg/l have been observed and the dominant species is usually complexed cyanide (Wild et al., 1994). In the Piedmont area of North Carolina, photographic developing, chemical, and furniture manufacturing plants are most likely to be major sources of cyanide, though their pretreatment process will normally remove the compounds prior to discharge from their plants.

2.5 Cyanide Treatment

Elevated levels of cyanide in industrial wastes have forced many utilities to impose discharge limits on industries so that the utility not only complies with its own discharge limit but is also able to limit exposure of the personnel working on the sewage collection system. Typical discharge limits from industries range from 5 mg/l to 10 mg/l (Lester, 1990).

The most common form of cyanide treatment utilized by industries to comply with the discharge permit is called alkaline chlorination. This process is a physical/chemical technique applicable for treatment of wastes containing up to 500 mg/l of cyanide (Ganczarczyk et al., 1985). This process involves the conversion of the cyanide into cyanogen chloride, CNCl, by the addition of the strong oxidant, chlorine (Kenfield et al., 1988).

$$NaCN + Cl_2 \rightarrow CNCl + NaCl$$

Cyanogen chloride is only slightly soluble, yet highly toxic gas; however, it will hydrolyze at high pHs to cyanate (CNO^-) which has a limited toxicity (APHA, 1995).

$$CNCl + 2NaOH \rightarrow NaCNO + NaCl + H_2O$$

The cyanate can be further oxidized with chlorine at near neutral pH to carbon dioxide and nitrogen.

$$2NaCNO + 4NaOH + 3Cl_2 \rightarrow 6NaCl + 2CO_2 + N_2 + 2H_2O$$

It is possible for the cyanate to be converted to ammonium ion upon acidification.

$$2NaCNO + H_2SO_4 + 4H_2O \rightarrow (NH_4)_2SO_4 + 2NaHCO_3$$

This chlorination process is fast for cyanide compounds that will dissociate readily. Since these are the compounds likely to be most toxic to aquatic life, many industrial discharge permits are governed by cyanide that is amendable to chlorination. This is simply the sum of the free cyanide and the complex cyanides that are readily dissociable under the chlorination process (APHA, 1995).

2.6 Wastewater Disinfection

Disinfection is the destruction of pathogenic organisms (Reynolds and Richards, 1996). This is not to be confused with sterilization, which is the destruction of all organisms (Metcalf and Eddy, 1991). The primary purpose of wastewater disinfection is to prevent the release of infectious agents to the environment (Metcalf and Eddy, 1991). The two most common types of disinfecting agents used in the United States for wastewater disinfection are chlorine and ultraviolet (UV) radiation (Reynolds and Richards, 1996).

2.6.1 Wastewater Chlorination

Chlorine is a strong oxidant. It may be applied as hypochlorite (OCl^-) or chlorine gas (Cl_2). Chlorine gas, upon the addition to water, will be converted into hypochlorous acid (HOCl). Hypochlorous acid is cheap and effective at low concentrations making it a widely used disinfecting agent (Reynolds and Richards, 1996). The degree to which chlorine will be effective to disinfect wastewater depends on several factors: time of contact, concentration, pH, number and type of organisms, nature of suspending liquid, and temperature. The longer the chlorine has to react with the microorganisms and the higher the chlorine concentration, the better the disinfection capacity.

Hypochlorous acid is a monoprotic acid with a pK_a=7.5 at 25°C. The pK_a is a function of temperature. The protonated form is a more effective disinfecting agent (40- 80 times better) making it necessary to have the wastewater stream's pH below the pK_a (Metcalf and Eddy,

1991). The number and type of organisms is an important parameter, since the need for overall disinfection is less with fewer microorganisms present in the wastestream and the effectiveness of chlorine is species dependent. Such organisms as *Cryptosporidium* oocysts have great resilience to chlorine. The nature of the wastewater has an impact on the effectiveness of the disinfecting agent. An example of this is the suspended solids content in the wastestream. Non-biological suspended matter can shield microorganisms from the chlorine or it can react with the chlorine directly (Reynolds and Richards, 1996).

Chlorine contact chambers are designed as plug flow reactors (Weber and DiGiano, 1996) to maximize the contact time. Consequently, the typical design pattern for chlorine contact chambers for wastewater treatment is a deep, baffled chamber causing a serpentine flow pattern as seen in Figure 2.1.

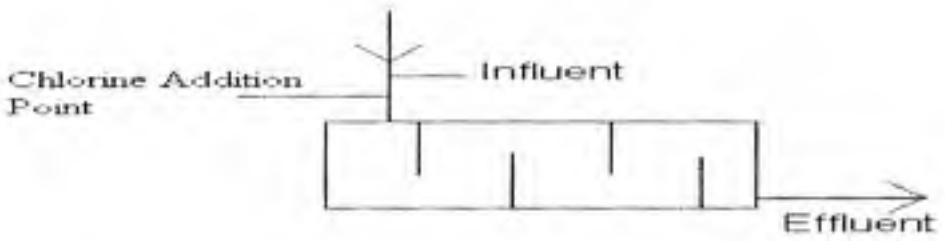

Figure 2.1 A Typical Schematic of a Wastewater Chlorine Contact Chamber in Plan View

2.6.2 UV Wastewater Disinfection

Irradiation with UV has been practiced in a limited form since the early 1900's for water supplies. Recent applications of UV for wastewater disinfection are at a wavelength of 254 nm (Reynolds and Richards, 1996). One of the most appealing advantages of UV is that there is no formation of toxic by-products such as are associated with chlorination (Metcalf and Eddy, 1991). UV is a physical agent as opposed to the chemical agent, chlorine, so the parameters are slightly different when rating the effectiveness of the disinfection capacity. In place of the notion of concentration, UV disinfection depends on the radiation dose. Other limiting factors associated with chlorination, such as pH and alkalinity, are not relevant with this form of disinfection. However, the suspended solids could shield and absorb the UV radiation similar to the effect described for chlorine.

The design of UV disinfection chambers maximizes the exposure of wastewater to the radiation. UV lamps are placed in arrays to minimize the distance from the microorganisms to the UV source, which in turn maximizes the effectiveness. Contact times are not as great as with chlorine, which reduces the tank size, but a high radiation dose is needed (Metcalf and Eddy, 1991).

2.7 Cyanide Analysis

2.7.1 Approved Methods for Total Cyanide Analysis

The most commonly employed methods for total cyanide analysis in wastewater are Standard Method 4500-CN^- (APHA, 1995) and EPA Method 335.2 (USEPA, 1978). The procedure detects cyanide in the aqueous sample by the use of a high temperature, low pH distillation reactor to break down all the complex cyanides. The cyanide is protonated into hydrogen cyanide, which volatilizes from the reactor through a condenser into a high pH absorption solution where it is retained in the free cyanide form. The cyanide is then converted into cyanogen chloride by reacting with chloramine-T and reacted with pyridine-barbituric acid to form a complex that can be analyzed colorimetrically. Figure 2.2 illustrates a typical digestion, distillation apparatus.

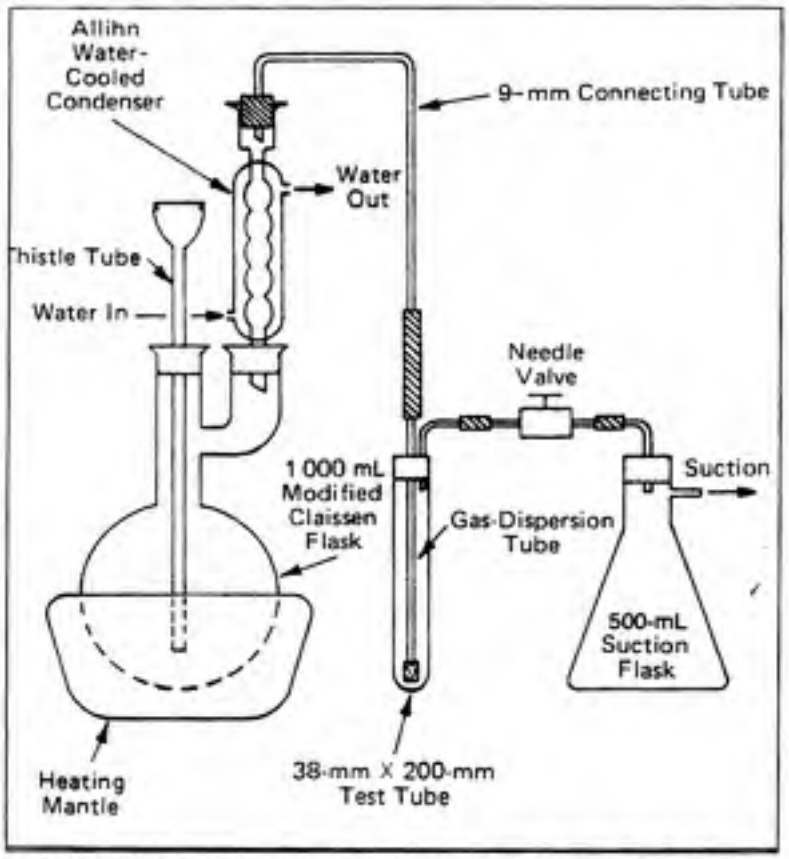

Figure 2.2 An Acid Distillation/Digestion Apparatus for Collection of Cyanide from Wastewater

A major disadvantage of this procedure is the long sample analysis times, typically 1.5 – 2 hours per sample. Multiple distillation apparatuses are required to analyze collected samples along with a calibration standards. Coupled with the long run times, quality assurance and quality control become difficult to perform. Spikes and duplicates of samples add significant amount of run times to the complete analysis of samples and are consequently rarely done.

This procedure also utilizes a high temperature, low pH solution during the distillation process (APHA, 1995). The testing involves the conversion of the cyanide into a more toxic cyanogen chloride, reaction with pyridine-barbituric acid, and the absorption solution is a high pH solution. This raises many safety concerns for laboratory personnel since a variety of toxic chemicals and hazardous conditions are present. Such precautions as performing this analysis in a hood and all personnel wearing protective clothing will help to alleviate this danger. However, complete safety of personnel is not possible.

Another approach for total cyanide analysis, listed as EPA Method 335.3, is an automated, ultraviolet digestion technique that employs the same chemistry as the Standard Method, but is set up as a flow injection system (EPA, 1978). Flow injection is a form of analysis that utilizes a

sample loop containing a set volume of the sample, which is regularly injected into a stream of reacting chemicals. This particular method uses some of the same chemicals as the distillation method and while reducing the sample run time and operator intervention, the method has trouble with the stabilization of the flow-through colorimetric cell, and many irregularities are reported with sample analysis.

2.7.2 Interference with Analysis

2.7.2.1 Residual Chlorine

For the analysis of post-chlorinated wastewater plant effluents, Standard Method 4500 CN^- for total cyanide analysis calls for the removal of any residual chlorine present in the sample (APHA, 1995). Approved, so-called chlorine quenching agents, include ascorbic acid, sodium thiosulfate and meta-arsenite (AsO_2^-). Sufficient quenching agent should be added so that all the residual chlorine is removed from the sample.

Residual chlorine can decompose many forms of cyanide in the wastewater samples (APHA, 1995). This makes removal of the residual chlorine imperative so that there are no cyanide transformations while the sample is being held for analysis or during analysis.

2.7.2.2 Sulfide

Sulfide (S^{2-}) is the most reduced form of sulfur in wastewater. It is usually present in anoxic waters due to the presence of sulfate reducing bacteria. Hydrogen sulfide is a diprotic acid (pK_{a1} = 7.05 & pK_{a2} = 14) that will be volatile at pHs well below the pK_{a1} and soluble at pHs well above the pK_{a1}. This allows it to volatilize and carry over with the cyanide in the Standard Method subsequently interfering with the colormetric measurement. In addition, sulfide and other sulfur compounds can react with cyanide to form thiocyanate, which is not captured as total cyanide and would therefore cause a negative bias in total cyanide measurement if this were to occur during sample handling and analysis (APHA, 1995). The suggested approach for sulfide removal from wastewater is the use of an agent that will precipitate the sulfide as an insoluble form which can then be removed through filtration with a 0.45 μm filter. One such agent is lead carbonate, $PbCO_3$. The solubility product of lead carbonate is 1.46×10^{-13} M^2 at 25 °C according to the following reaction (CRC, 1995).

$$PbCO_3(s) = Pb^{2+}(aq) + CO_3^{2-}(aq)$$

The dissolved lead species is then involved with a reaction with sulfide as listed below. The equilibrium constant for this reaction is 10^{-27} M^2 at 25 °C (CRC, 1995).

$$PbS(s) = Pb^{2+}(aq) + S^{2-}(aq)$$

These reactions will result in sulfide removal from the sample since the precipitated form of sulfide is physically removed from the sample. Only an extremely small amount of sulfide will remain in solution, which corresponds to the concentration of dissolved sulfide that will be in equilibrium with the precipitated form. The Standard Method 4500-CN indicates that the presence of sulfide can be identified by lead acetate strips. These strips are inadequate for low level detection of sulfide. The limit of accuracy is greater than 1 mg/l, so sulfide concentrations below this limit will not be detected by these strips.

2.7.2.3 NITRITE

Nitrite (NO_2^-) is an intermediate product of nitrification and denitrification that is associated with the oxidation and reduction cycling of nitrogen in the environment (Metcalf and Eddy, 1991). Recent articles and reports have suggested that nitrite may be involved in a cyanide formation reaction with certain components of wastewater (Carr et al., 1994; Rapean et al., 1980).

In particular, when Carr et. al chlorinated a synthetic water containing ammonia and subsequently used ascorbic acid to quench residual chlorine, they measured elevated levels of cyanide and nitrite that were not present when one of these components was absent. In other experiments, the chlorine was not allowed to react with the ammonia, which did not cause a formation of cyanide or nitrite. A correlation was therefore found between nitrite (or other sources of nitrogen) concentration, subsequent chlorination, and the use of ascorbic acid as the quenching agent (a source of carbon for the cyanide). Ascorbic acid is among the most common quenching agents due to its non-toxicity to laboratory personnel.

The Standard Method procedure for removal of nitrite is the addition of sulfamic acid, NH_2SO_3H, to the sample immediately before analysis of the sample (APHA, 1995). Sulfamic acid reacts with nitrite in solution in the following way (Woods and Holliday, 1967):

$$NH_2SO_3H(aq) + NO_2^-(aq) \rightarrow N_2(g)\uparrow + HSO_4^-(aq) + H_2O(l)$$

Nitrite, in a strongly acidic solution such as is present during distillation of the wastewater in preparation for cyanide analysis, can protonate to nitrous acid (HNO_2). This protonated form of nitrite was hypothesized to be responsible for cyanide formation. Since this was the agent responsible, the need to remove the nitrite was not required by Standard Method 4500-CN until immediately before analysis, and not at the time of sample collection.

Carr (1994) also observed that the cyanide concentration was two to three times greater in deionized (DI) water samples that were spiked with nitrite and ascorbic acid, stirred, then denitrified with excess sulfamic acid as opposed to DI water samples that were spiked with nitrite, denitrified, and then spiked with ascorbic acid. This adds further credence to the suggestion that a reaction of nitrite with a carbon source may be a pathway for cyanide formation. Other organic compounds commonly found in wastewater were tested to see if cyanide formation occurred in the presence of nitrite. The compounds glucose, sucrose, starch, cellulose, and alcohol indeed appeared to provide the carbon source for cyanide formation. A table summarizing the results of the Carr study is given below in Table 2.1. Each organic constituent was added at 10 mM in a DI solution containing 10 g/L of sodium nitrite as nitrite. The resulting cyanide concentration is given together with its respective solution components.

Table 2.1 A Summary of the Cyanide Levels Formed by Reaction of Nitrite and Various Organic Precursors (Carr et. al. 1994)

Carbon Source (10 mM)	[CN^-] (ppm)
Methanol	0.035
Ethanol	4.17
n-Proply alcohol	112
i-Proply alcohol	56.9
t-Butanol	51.5
Formic Acid	0.34
Acetic Acid	0.04
Oxalic Acid	0.063
Citric Acid	0.068
Tartaric Acid	0.027
Ascorbic Acid	10.7
D-Ribose	0.661
Sucrose	5.64
Mannitol	0.991
Dextrose	0.319
Starch	0.228
Methyl Cellulose	0.007
Tissue Paper (Kimwipes)	0.084
2-(5H)Furanone	33.6
2-Furaldehyde	29.2
Urea	0.139
Acetonitrile	0.189
Sulfamic Acid	<0.002

CHAPTER 3

MATERIALS AND METHODS

3.1. GLASSWARE

Forty milliliter glass vials, that were used for the cyanide and nitrite analysis, were rinsed with tap water, soaked in a 10% nitric acid (certified A.C.S. plus grade, Fisher Scientific, Pittsburgh, PA) bath overnight, rinsed three times with deionized (DI) water (Dracor Inc., Durham, NC), and dried in an oven (Fisher Scientific, Pittsburgh, PA) at 100°C. All other laboratory glassware used for analysis and sample collection, except for volumetric glassware underwent the same cleaning procedure. All volumetric laboratory glassware underwent the same cleaning procedure except for the oven drying process. To prevent damage to the accuracy of the volumetric calibration of the glassware, the volumetric glassware was dried at room temperature inverted over clean utility wipes (Scott Paper Company, Philadelphia, PA). The 1-L polypropylene bottles, used for sample collection, were cleaned by first soaking in an Alconox bath (Alconox Inc., New York, NY). The bottles were then rinsed with tap water and soaked in a 10% nitric acid bath. Finally, the bottles were triple rinsed with DI water and dried by inversion over clean utility wipes.

3.2 SAMPLE COLLECTION

3.2.1 NATURE OF PARTICIPATING UTILITIES

Four wastewater utilities in North Carolina, all practicing post-chlorination, were sampled in this study – Burlington, High Point, Greensboro, and Winston-Salem. Each utility was sampled once with the exception of the High Point utility where a second sampling trip was organized. Each utility has two plants treating the municipal wastewater, both of which were sampled during this study. Table 3.1 lists the comprising plant for each utility along with the discharge permit at each plant. All of these plants use a nitrifying, activated sludge for compliance with the oxygen demand and the ammonia permit requirements. To comply with enhanced nutrient removal, these plants utilize tertiary filtration with the exceptions of Muddy Creek and North Buffalo.

Table 3.1 The Treatment Plants and the Cyanide Permit Levels for the Sampled Utilities

Utility	Comprising Wastewater Treatment Plants	Cyanide Discharge Permit Level (ppb as CN^-)
Burlington	East Burlington	5
	South Burlington	5
High Point	Eastside	5
	Westside	5
Greensboro	T.K. Osborne	10
	North Buffalo	10
Winston-Salem	Archie Elledge	6.6
	Muddy Creek	Not Applicable

3.2.2. Sample Collection Points

Grab samples were collected in 1-L polypropylene bottle (Fisher Scientific, Pittsburgh, PA) at three different points in the wastewater treatment process. The first sample collection point was immediately before the point of chlorination to provide an opportunity to measure the wastewater quality prior to chlorination. The second point was immediately after the chlorine was added to the wastewater. This was done to capture the maximum impact of the chlorine before any chemical changes could occur with the contact time of the chamber. The third sample was collected at the effluent point of the plant, the point at which samples are collected for monitoring compliance with the effluent cyanide permit. The timing of sample collection on this project was coordinated with the weekly sample collection by the utility so that sample analysis at UNC could be compared with the currently practiced procedure for compliance monitoring by the utility. A schematic illustration of the sample collection points at the wastewater treatment plants is given in Figure 3.1.

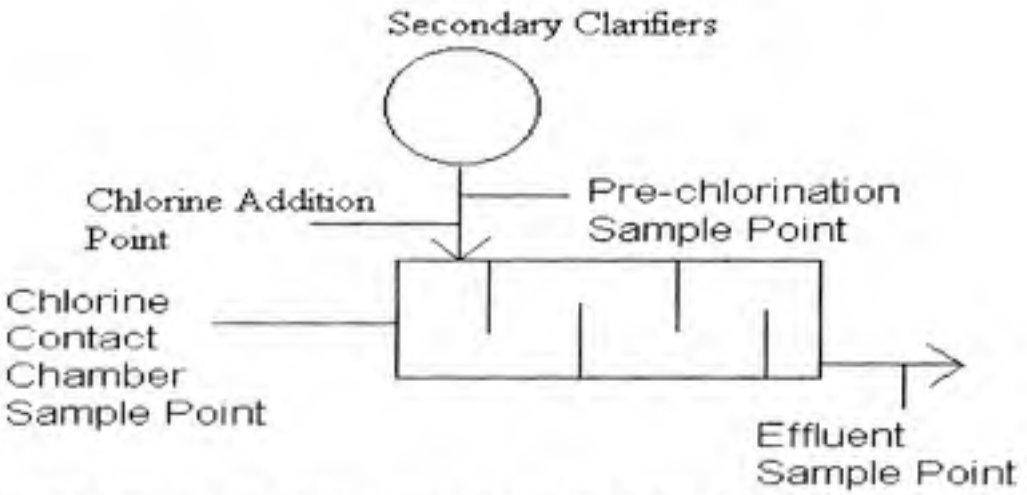

Figure 3.1 Schematic of the Sample Collection Points in the Wastewater Treatment Chlorination Process

3.2.3 Laboratory Chlorination

An additional 500 ml of the prechlorinated wastewater was poured into a 500-ml volumetric flask for subsequent controlled chlorinations at the UNC-CH laboratories. Information was collected on-site about chlorine doses to duplicate conditions at the wastewater treatment plants in the laboratory. Appropriate dilutions of the stock chlorine solution to the 500-ml of wastewater were made in order for the correct chlorine dose to be applied. The chlorinated laboratory samples were gently stirred in the light for 15 minutes, which is similar to the conditions found in the plants.

3.2.3.1 Chlorine Calibration Procedure

Sodium hypochlorite, NaOCl, (Aldrich, Milwaukee, WI) was used as the chlorine source in laboratory chlorinations and was calibrated before use each time. The procedure was used to determine the chlorine concentration of the stock solution which was labeled as >4%. The procedure as outlined in Standard Method 408 A involves two separate titrations involving thiosulfate and dichromate (APHA, 1995).

The thiosulfate is standardized by titrating against a 0.1 N potassium dichromate ($K_2Cr_2O_7$) solution (Aldrich, Milwaukee, WI). The chlorine is titrated against a 0.1 N sodium thiosulfate ($Na_2S_2O_3$) solution (Fisher Scientific, Pittsburgh, PA). The thiosulfate and chlorine solutions are known not to be completely stable for long periods, whereas, potassium dichromate solutions are very stable for extended periods.

3.2.3.1.1 THIOSULFATE STANDARDIZATION

In a clean beaker, 1 ml of concentrated sulfuric acid (Fisher Scientific, Pittsburgh, PA), 10 ml of 0.1 N potassium dichromate solution, and approximately 80 ml of DI water were added. Approximately 1 g of potassium iodide (Fisher Scientific, Pittsburgh, PA) and 1 ml of a 5.6 g/l starch solution were then placed into the beaker (Fisher Scientific, Pittsburgh, PA) and allowed to dissolve in the dark. The solution in the beaker was then titrated with sodium thiosulfate solution to its endpoint and the volume of thiosulfate solution titrated was used to calculate its concentration by using the following formula.

$$N_{thiosulfate} = \frac{N_{dichromate} \times V_{dichromate}}{V_{thiosulfate}}$$

where N is the normality of the specific solution in units of equivalents per liter and V is the volume of the solution added in units of liters. Although the original thiosulfate solution was prepared at 0.1 N, degradation necessitates periodic calibration by this procedure.

3.2.3.1.2 CHLORINE TITRATION

A 1:10 dilution of the chlorine stock solution was prepared in a volumetric flask. In a clean beaker, 5 ml of glacial acetic acid (Fisher Scientific, Pittsburgh, PA) and approximately 1 g of potassium iodide was added while stirring. Ten milliliters of the 1:10 diluted chlorine solution was then placed into the beaker and the mixture was titrated with 0.1 N sodium thiosulfate. Prior to the endpoint to permit more precise titration, 1 ml of the starch solution was added. The normality of the diluted chlorine solution was determined as follows.

$$N_{1:10diluted_{Cl_2}} = \frac{N_{thiosulfate} \times V_{thiosulfate}}{V_{1:10diluted_{Cl_2}}}$$

where N is the normality of the specific solution in units of equivalents per liter and V is the volume of the solution added in units of liters. The normality of the stock solution was ten times this normality.

In addition, conversion from normal units (eq/l) to units of mg/L must be employed. A summary of these conversions is given in the following formula:

$$Concentration_{stock_{NaOCl}} = N_{Undiluted_{NaOCl}} \times 10 \times \frac{1mol_{Cl_2}}{2eq_{NaOCl}} \times \frac{2mol_{Cl}}{1mol_{Cl_2}} \times \frac{35.45g_{Cl}}{1mol_{Cl}} \times \frac{1000mg}{1g}$$

where the concentration is in unit of mg/l and the normality term is in units of eq/l.

3.3. Sample Treatment Procedures

Cyanide analysis on collected samples involves two steps. The first step is to stabilize and preserve the sample so that there are no cyanide transformations while the sample is being held for analysis. The second step is the analytical method employed for cyanide analysis. Several stabilization procedures were employed in this study, but the cyanide determinations on those stabilized samples were performed in the same manner.

3.3.1 Sample Stabilization Procedures

All wastewater samples must be stabilized and preserved in order to be accurately analyzed for cyanide. Since chlorine, sulfide, and nitrite were considered as major sources of cyanide destabilization, procedures for their removal were employed. Stabilization of the samples refers to preventing conditions that would cause an unwanted impact on the cyanide concentration for analysis procedure, whereas, preservation refers to the use of chemical agents to prevent any loss of cyanide through volatilization. All stabilization and preservation procedures were employed on site immediately after sample collection at the wastewater treatment plants. A flow diagram of the stabilization procedures used is given below as Figure 3.2.

All of the stabilization procedures involve the removal of chorine. One of the stabilization procedures only involves chlorine quenching. The other stabilization procedures were to remove the sulfide and to remove the nitrite. A procedure was developed to quench the chlorine and to remove the sulfide, while another procedure involved chlorine quenching and nitrite removal. The fourth stabilization procedure employed chlorine quenching, sulfide removal, and nitrite removal. After the sample was stabilized, it was preserved according to the procedure explained below.

3.3.1.1 Chlorine Quenching

The first stabilization procedure was to quench the chlorine with sodium meta-arsenite, Na_2AsO_2, (J.T. Baker, Phillipsburg, NJ)). An aliquot of the wastewater sample was placed in

the 40-ml vial until head-space free which contained 80 μL of 11.3 g/L of sodium meta-arsenite as meta-arsenite. The vial was capped and mixed. This amount of meta-arsenite has the capacity to quench 15 mg/l of chlorine as Cl_2.

3.3.1.2 Sulfide Precipitation

The next stabilization procedure involved precipitating sulfide from the sample. An aliquot of a wastewater sample was placed into a 40-ml vial, which contained a small quantity (~150 mg) of lead carbonate (Aldrich, Milwaukee, WI) until head-space free. The sample was capped and mixed. The sample was then immediately filtered, to remove the precipitated sulfide, using a syringe (Becton Dickinson & Co., Franklin Lakes, NJ) and a 0.45 μm nylon syringe filter (Nalge Co., Rochester, NY) which connect together by means of a leur lock. Twenty milliliters of the filtered sample was collected in a clean glass vial.

3.3.1.3 Nitrite Removal

The third stabilization procedure involved the removal the nitrite from the wastewater sample. An aliquot of a wastewater sample was placed into a 40-ml vial, which contained 80 μL of 6.35 g/L sulfamic acid (Aldrich, Milwaukee, WI) until head-space free. The sample vial was capped and mixed. At this given dose, the sulfamic acid has the capacity to remove 6.00 mg/L of nitrite.

3.3.2 Sample Preservation

After every stabilization procedure, the sample must be preserved to prevent the loss of cyanide through volatilization. Free cyanide is very soluble at high pHs well above the pK_a (9.2) of free cyanide. In order to raise the pH to a value that will prevent volatilization, 200 μL of 50% w/w NaOH was added to the unfiltered samples. If the sample was filtered to remove sulfide, 100 μL of 50% w/w NaOH was added to account for the lower collected sample volume. The wastewater sample pH after the addition of sodium hydroxide was approximately 12. The sample vial was capped and mixed. All samples were then stored at 4°C in a refrigerator until analysis was performed.

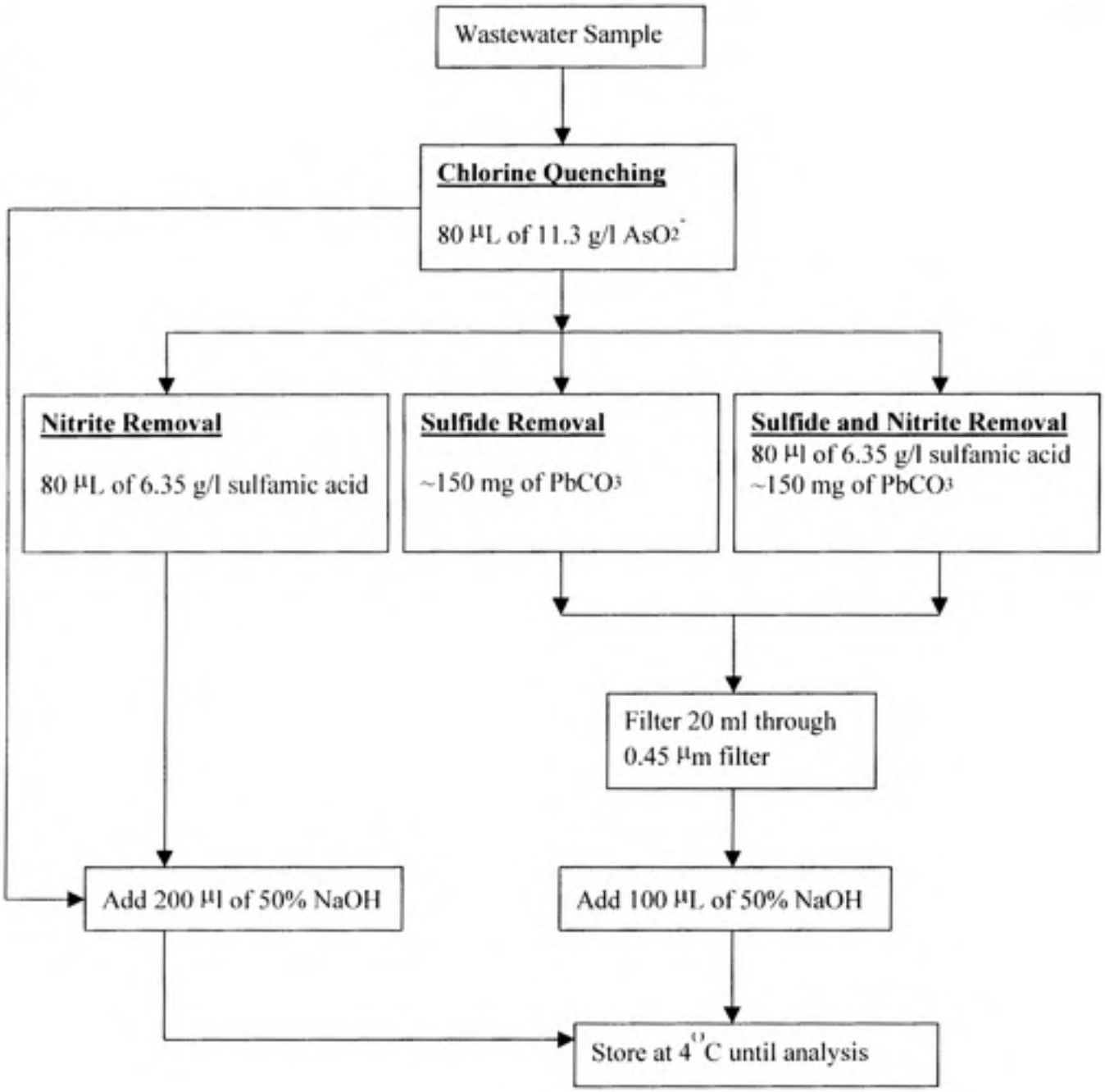

Figure 3.2 Process Flow Diagram of the Stabilization and Preservation Procedures Used

3.3.3 Application of Stabilization Procedures to Samples Collected by Utility for Permit Requirements

An approach to incorporate the stabilization techniques into routine sample analysis using the tradition Standard Method 4500-CN is given in Appendix A.

3.4 Cyanide Analysis Procedure

The CNSolution 3202 (Alpkem, Wilsonville, OR) flow injection analyzer was used for total cyanide concentration determinations as outlined in Figure 3.3. This automated procedure permits the generation of an analytical response much quicker than the method outlined in Standard Methods. Instead of a sample taking 2 hours to complete as in the Standard Methods, a sample could be analyzed every 210 seconds. The cyanide analyzer was also equipped with an autosampler to allow many samples to be tested. This allows more testing of samples in a faster time. In addition, more quality assurance and quality control is available to the user. Most previously documented applications of this instrument have been to cyanide determinations in mining wastes, not to municipal wastewater. Since mining wastes are dominated by complex cyanides, application of this method to wastewater was explored in this research.

The aqueous sample is first loaded into a 200-µl sample loop and then switched in-line with a carrier solution as a segmented plug of sample within the carrier solution stream. The sample is acidified, aerated, and then irradiated by ultraviolet light to decompose the metal-cyanide complexes into free cyanide in a digester. The wavelength of the digester is specifically set to break down complex cyanides but not thiocyanate. The sample plug is acidified again to convert the degraded cyanide into volatile hydrogen cyanide, which then passes through a gas diffusing membrane where the gas rises to separate from the carrier solution. The hydrogen cyanide then joins another stream of base reagent which converts the volatile hydrogen cyanide into the soluble cyanide ion (CN^-).

This stream passes into an amperometric detector optimized for cyanide analysis. The response of the detector is continuously monitored by a computer and is graphically represented as a peak on the output showing resulting current (pA) as a function of time. An example of this output for a wastewater sample analyzed to have a total cyanide concentration of 18.5 ppb is given as Figure 3.4.

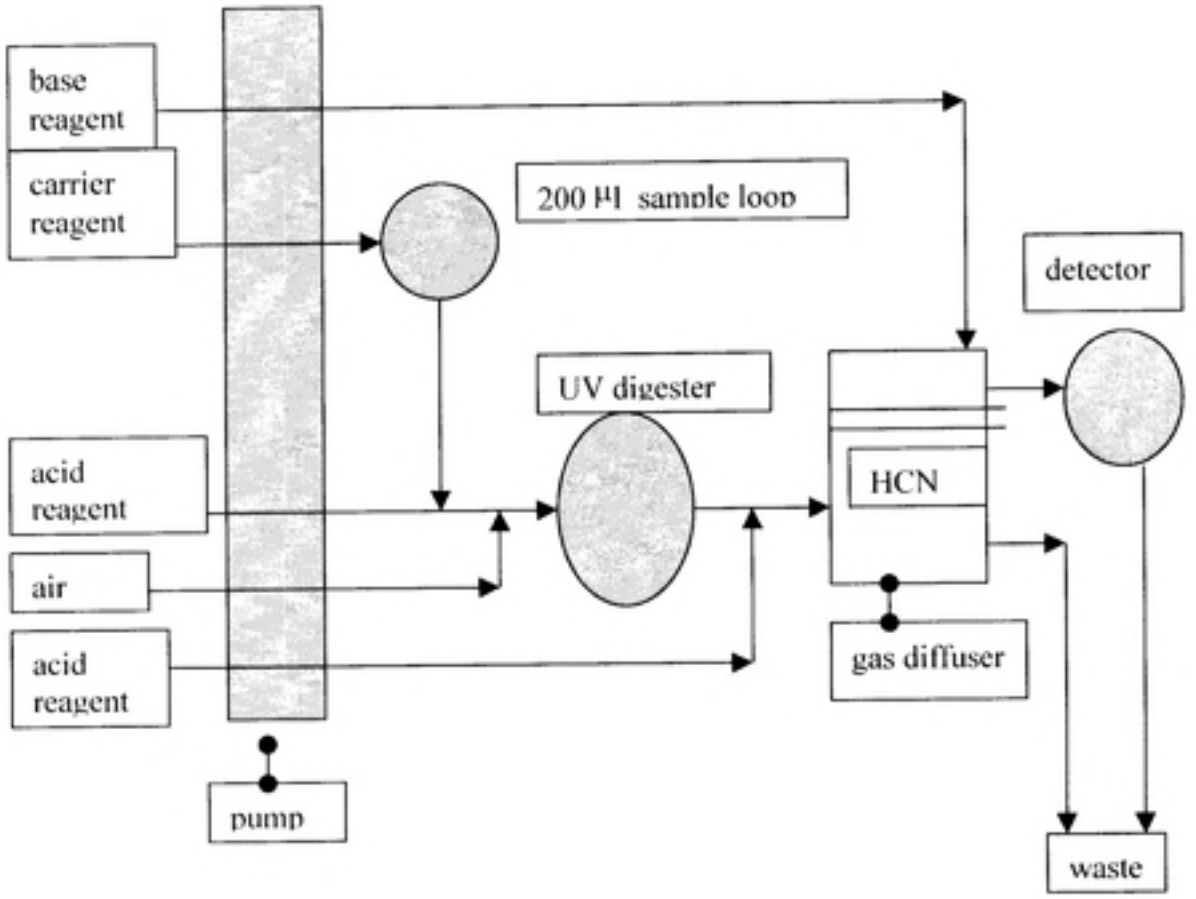

Figure 3.3 A Flow Diagram of the Cyanide Analyzer

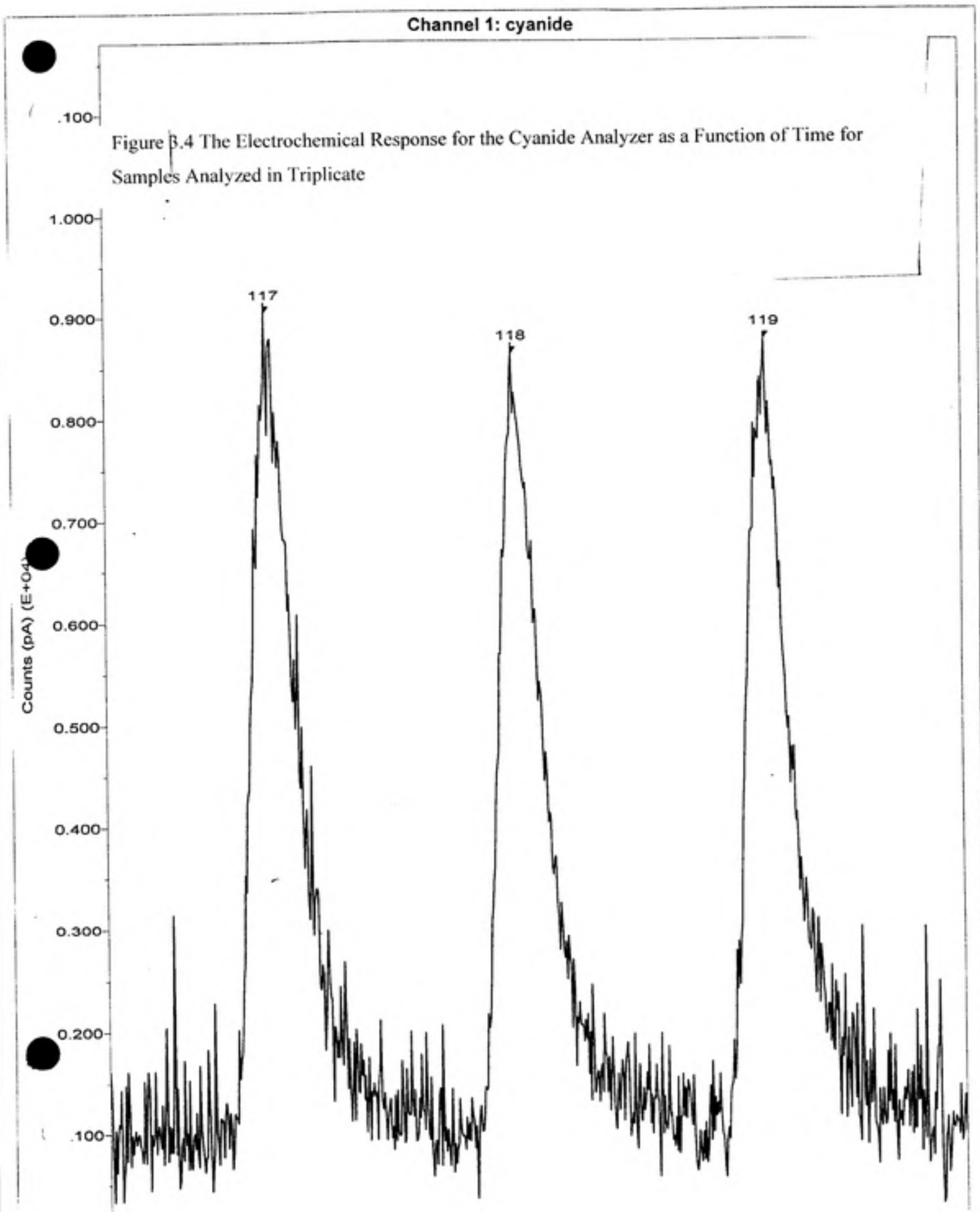

Figure 3.4 The Electrochemical Response for the Cyanide Analyzer as a Function of Time for Samples Analyzed in Triplicate

3.4.1 Total Cyanide Calibration Curve

To determine total cyanide (TCN) concentrations in wastewater samples, a relationship between the response of the instrument to a given total cyanide concentration must be developed. A seven point calibration curve (0 – 25 ppb TCN as CN^-) was analyzed by the flow injection made from a stock solution containing both free (48 mg/l) and complexed (54 mg/l) cyanide (Inorganic Ventures, Inc., Lakewood, NJ). The free cyanide was potassium cyanide (KCN), while the complex cyanide constituent was potassium ferricyanide ($K_3Fe(CN)_6$). The total cyanide concentration is then 102 mg/l. The sample matrix for all calibrants was 0.1 N sodium hydroxide (NaOH). The response of the known calibrants was graphed against the calibrants concentration. A best fit regression line was determined from the generated data. Validation of the regression equation was done by inspection of the correlation coefficient (R^2). The regression equation was used to determine unknown total cyanide concentration by substitution of the instrument response to yield the total cyanide concentration. Analysis of 0.1 N NaOH yields a positive response in the total cyanide flow injection analyzer; consequently, a positive y-intercept in the regression equation was allowed. The positive response is believed to be caused by sulfide contamination of the 50% (w/w) sodium hydroxide stock solution (Fisher Scientific, Pittsburgh, PA) during storage of the stock solution.

The sample matrix for all calibrants was 0.1 N sodium hydroxide made in DI water. A primary dilution of the total cyanide stock standard was made to make the total cyanide calibrants. Four hundred ninety microliters of the 102 mg/l total cyanide stock solution was placed into 25 ml of 0.1 N NaOH. The primary dilution was then used to make all the calibrants as outlined in Table 3.2.

Table 3.2 The Procedure Used to Make the Total Cyanide Calibration Curve

Calibrant Concentration (μg/l as CN^-)	Volume of Calibrant (ml)	Volume of Primary Diluent Added (μl)
0	50	0
2	50	50
5	50	125
10	50	250
15	50	375
20	50	500
25	50	625

3.5 Nitrite Analysis

As implied in the work of Carr et al. (1994), nitrite is likely to be involved in a cyanide transformation occurring in the sample analysis procedure. Determination of nitrite concentration in the pre-chlorination wastewater sample is thus important to characterize the potential for possible cyanide formation. The method selected for nitrite analysis will however only measure dissolved nitrite. Any nitrite associated with the solid particles found in wastewater is filtered out prior to analysis. Since all the wastewater samples are collected after secondary clarification, the nitrite associated with suspended material is believed to be negligible.

3.5.1 Sample Preparation

3.5.1.1 Stabilization

Nitrite in wastewater is not stable (Metcalf and Eddy, 1991). Wastewater treatment plants are often required to practice nitrification, conversion of ammonia to nitrate through biological activity, to comply with effluent discharge permits. Since nitrite is an intermediate in this process, wastewater samples collected from plants that practice nitrification are likely to contain nitrite in a state of flux even if the sample is collected after the biological treatment reactors and clarifiers. In order to preserve the collected samples, they were stored at 4°C until analysis was performed within 48 hours of sample collection. This reduces the chance for further nitrification to occur by reducing the nitrite oxidation rate of the microorganisms and shortening the time allowed for nitrification.

3.5.1.2 Suspended Solids

The analytical method for nitrite, ion chromotagraphy (IC), requires that all samples be free of suspended solids. This is achieved by filtering the wastewater samples through a 0.45 μm nylon syringe filter (Nalge Co., Rochester, NY).

3.5.1.3 Removal of Chloride Interference

Chloride is an interferant with nitrite analysis by IC. Chloride concentrations in wastewater can be high (>100 mg/l). These levels can conceal the nitrite content of the wastewater. The analytical method for nitrite requires the chloride impact be removed to fully determine the nitrite concentration. The method used for chloride removal in the wastewater samples was the use of OnGuard silver resins (Dionex, Sunnyvale, CA) that retain the chloride as silver chloride. The previously filtered wastewater sample was passed through the resin by an automated sample

loader at a speed optimized to maximize the removal of chloride. The resin eluate was collected in an autosampler vial for subsequent analysis of nitrite.

3.5.1.4 Filtration Procedure

To remove the suspended solids, the wastewater sample was loaded into a disposable, plastic syringe (Becton Dickinson & Co., Franklin Lakes, NJ) which was equipped with a Leur lock. The 0.45 μm nylon syringe filter was attached to the syringe. Two OnGuard silver resins were attached in series at the end of the 0.45 μm nylon syringe filter to remove the chloride. The syringe and attached syringe filters were placed in a syringe pump (Harvard Apparatus, South Natick, MA). This press passed the sample through the filters at a slow rate (2 ml/min) so that the chloride had sufficient time to be removed in the silver resins.

3.5.2. Nitrite Analysis Procedure

All nitrite analysis was performed on a Dionex Model DX300 ion chromatograph with detection by conductivity (Dionex, Sunnyvale, CA). IC utilizes the ion exchanging capabilities of specific resins to separate the component ions and subsequently elute ions at distinctly separate retention times. The resolved anions are converted into their conjugate acids which are more highly conductive than their corresponding salts and which permits detector sensitivity at the sub nano-molar level. This is accomplished through use of an anion micromembrane suppressor and a countercurrent flow of 200 mN sulfuric acid.

A filtered and chloride-free wastewater sample is loaded into a 150-μL sample loop which is subsequently switched in-line with the carrier eluent. An AS10 guard column preceded the analytical AS10 column, which performs the anion exchange process with the aid of sodium hydroxide mobile phase. At a flow rate of 1.0 ml/min, eluents of 10 mN NaOH and 200 mN NaOH were used in combination to first eluate the nitrite ion and then subsequently by raising the eluent concentration. The remaining ions in the sample were swept from the column thereby preparing it for the loading of the next sample.

The eluted suppressed ions emerging from the suppressor generate a response in the conductivity detector which contributes to the generated chromatogram. Individual peaks are integrated by Peaknet Software (Dionex, Sunnyvale, CA) and reported peak heights are directly proportional to the component concentration. The overall scheme for the IC procedure is shown in Figure 3.5.

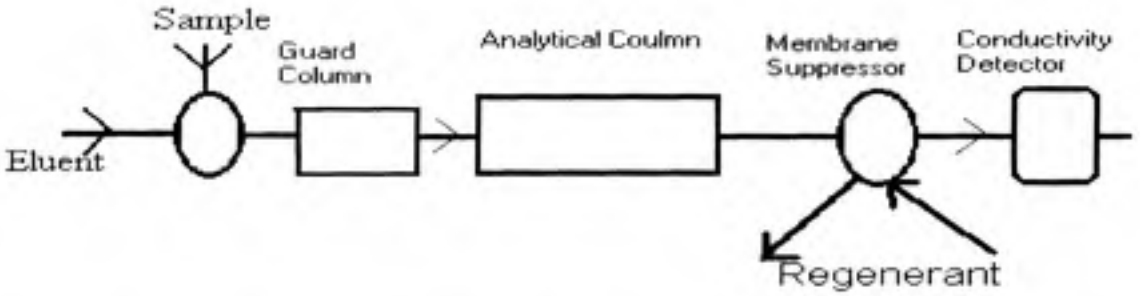

Figure 3.5 A Flow Diagram of the Nitrite IC Analysis

A total run time of 30 minutes was needed in order to clean the column of all anions for the next sample, although, the nitrite ion was observed at a retention time of 10.5 minutes. As a sample run proceeded, more of the higher concentration eluent was used to wash the anions off faster in a gradient elution mode. A table summarizing the eluent gradient is given below in Table 3.3. A sample chromatogram for a wastewater sample that was analyzed to be 450 ppb nitrite is given below as Figure 3.6.

Table 3.3 A Summary of the Eluent Gradient for Nitrite IC Analysis

Time (min)	% of 10 mN NaOH	% of 200 mN NaOH used
0	92	8
20	92	8
23	10	90
26	92	8
30	92	8

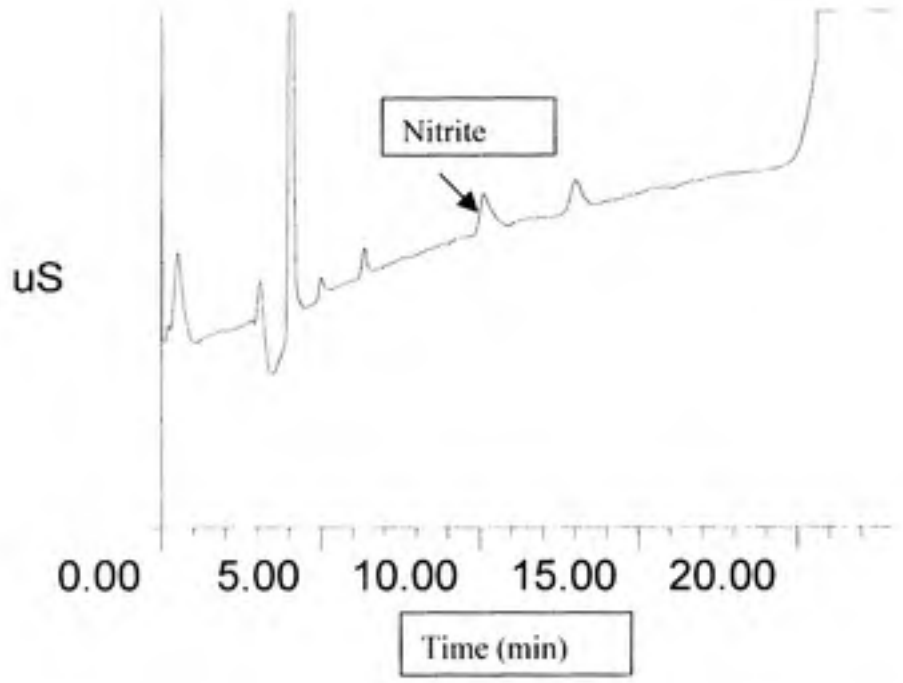

Figure 3.6 Sample Chromatogram for Nitrite Analysis for a Wastewater Sample

3.5.2.1. CALIBRATION CURVE

To determine unknown nitrite concentration in samples, a calibration curve was used. A calibration curve was generated by plotting the response of an analytical method to known concentrations of standards against the standard concentration. The standards were made in a deionized water matrix. A regression line was determined from the data according to the least squares method. The equation of this regression line can be used to determine unknown sample concentrations by substitution of the instrument response for such samples to yield the concentration of the same sample. A zero point calibration sample represents the response to deionized water and for this particular method should be zero, thus allowing the calibration curve to be regressed through the origin.

The calibrants were prepared from dilutions of stock solution of nitrite made from sodium nitrite powder (Mallinckrodt Chemicals, Paris KY). The stock solution was made by adding 187.5 mg to 100 ml of DI water to yield a 1250 mg/l sodium nitrite solution as nitrite. A primary dilution was prepared from a 1:25 dilution of the stock solution. Specifically, this was achieved by adding 1 ml of the 1250 mg/l stock solution to 25 ml of DI water. The calibrant concentrations were prepared as described in Table 3.4.

Table 3.4 Preparation of Nitrite Calibrants Solutions

Calibrant Concentration (µg/l)	Total Volume of Calibrant (ml)	Volume of Primary Dilution Added (µl)	Volume of Stock Solution Added (µl)
0	100	0	--
10	100	20	--
25	100	50	--
50	100	100	--
100	100	200	--
500	100	--	40
1000	100	--	80

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SUMMARY OF TOTAL CYANIDE CALIBRATION CURVES

A seven-point calibration curve (0 – 25 ppb TCN) for total cyanide was analyzed for each sample run by flow injection analysis. The calibrants were made from a stock solution containing both free cyanide and complexed $(Fe(CN)_6)^{3-}$ cyanide. The solution matrix for the calibration standards was 0.1 N sodium hydroxide. The response for each calibrant was plotted against the calibrant concentration to yield a calibration curve. A best-fit regression line was determined from the data. The resulting regression equation was used to determine cyanide concentration in the wastewater samples. The correlation coefficient (R^2) was determined for each sample run, which indicates the goodness of the regression fit and its resulting use of interpolation. The graphical representation of a sample total cyanide calibration is given in Figure 4.1. A summary of the calibration curve's slope, y-intercept, and the correlation coefficient are given in Table 4.1 to demonstrate the variability of the instrument response for each sample run.

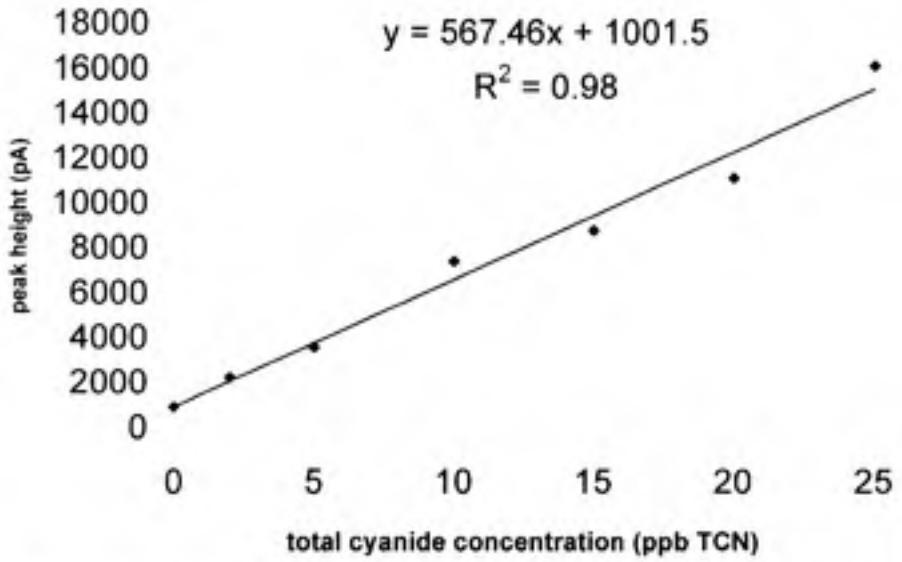

Figure 4.1 A Total Cyanide Calibration Curve for the South Burlington Wastewater Samples

Table 4.1 A Summary of all Total Cyanide Calibration Curves for Collected Wastewater Sample

Sample Site	Slope (pA•L/μg)	Y-Intercept (pA)	R^2
Impact of meta-Arsenite Experiments*	573.8	768.14	0.9987
South Burlington (Round 1)	567.46	1001.5	0.98
East Burlington (Round 1)	463.16	628.39	0.9982
High Point (Round 1)	382.78	314.71	0.9955
Greensboro (Round 1)**	227.62	454.4	0.997
Winston-Salem (Round 1)***	401.67	935.13	0.9992
High Point Eastside (Round 2)	393.46	1039.9	0.9967
High Point Westside (Round 2)	462.77	186.47	0.9747

* - Four Point Calibration Curve (0, 5, 10, and 50 ppb TCN as CN^-)
** - 25 ppb TCN calibrant was not included in regression analysis
*** - 0 ppb TCN calibrant was not included in regression analysis

The first observation is that the addition of sodium hydroxide to a DI water sample, as seen in the zero point of the calibration curve, caused a slight positive response for the flow injection total cyanide analyzer. This positive bias is reflected in all samples to which sodium hydroxide is added suggesting that the latter is a source of contamination, most likely sulfide, which produces a response similar to cyanide in the total cyanide analysis procedure. The sulfide contaminated the stock sodium hydroxide solution by dissolving from the gaseous phase. Due to the extremely high pH of the hydroxide solution, gaseous hydrogen sulfide (H_2S) will enter into this solution to obtain a chemical equilibrium. The hydrogen sulfide will deprotonate into the ionic specie, S^{2-}, in the aqueous solution. This bias is represented by the intercept on the y-axis of the calibration curve.

The slope of the various calibration curves ranges from 228 – 573 pA•L/μg. This is a small range, which indicates that there is reproducibility, sensitivity, and calibration of the response over time with this method. The y-intercept ranges from 186 – 1001 pA. This indicates the varying degrees of sulfide contamination in the calibrant matrix. Special measures should be employed to use sodium hydroxide that is as uncontaminated as possible.

4.2 Summary of Nitrite Analysis Calibration Curves

A six-point calibration curve was employed to determine the nitrite concentration in unknown wastewater samples as analyzed by ion chromatography (IC). The calibrants were made in DI water as outlined in Chapter 3 to the following concentrations – 10, 25, 50, 100, 500, and 1000 ppb nitrite (NO_2^-). A blank of DI water was analyzed. The response of the instrument, peak

height, was plotted against the calibrant concentrations. A blank consisting of DI water was also analyzed and included in the regression analysis. There was no response of the instrument to this blank, so the regression equation for the calibration curve was forced through the origin. The resulting correlation coefficient was calculated to rate the goodness of fit. The correlation coefficient was 0.999 for all the calibration curves. This is extremely high, so the instrument response was concluded to be a linear function of the calibrant concentration. A sample calibration curve is given below in Figure 4.2, while a summary of all the calibration curves, presented in Table 4.2, demonstrates the variability of the instrument response for each of the sample runs. The practical quantification limit for this method was determined empirically to be 40 ppb.

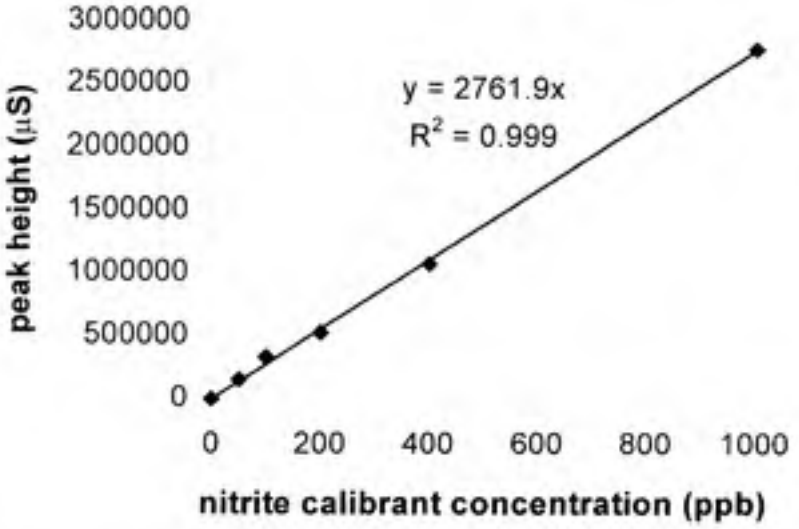

Figure 4.2 Nitrite Calibration Curve for the First Round of Sampling of the Burlington, High Point, and Greensboro Wastewater Samples

Table 4.2 A Summary of the Calibration Curves Used for Nitrite Concentration Determination in Wastewater Samples

Sample Site	Slope ($\mu S^{\bullet} L/\mu g$)	R^2
Burlington, High Point, and Greensboro (Round 1)	2761.9	0.999
Winston Salem (Round 1)*	3885.9	0.999
High Point (Round 2)*	3430.0	0.999

* - 1000 ppb calibrant was not included in regression analysis

4.3 Impact of meta-Arsenite on Total Cyanide Concentrations

In order to ensure that meta-arsenite does not impact the total cyanide concentration, a variety of solution matrices were analyzed. The total cyanide concentration was determined through flow injection analysis, and the resulting impacts were determined through comparison to other solution matrices analyzed.

Meta-arsenite is not typically employed as a quenching agent in laboratory practice due to its toxicity to humans. It is, however, an approved quenching agent for the Standard Method for total cyanide analysis of wastewater (Standard Method 4500-CN) along with ascorbic acid and thiosulfate (APHA, 1997). The appeal of meta-arsenite derived from Carr's (1994) work on interference of ascorbic acid and possible degradation of thiosulfate into sulfide in the UV digester of the flow injection analysis total cyanide analyzer.

The solution matrices analyzed in this experiment were 0.1 N sodium hydroxide (NaOH), chlorinated 0.1 N NaOH, high pH (>12) wastewater, and chlorinated high pH (>12) wastewater. Any chlorine quenching was done through the addition of meta-arsenite. A summary of the samples analyzed and their associated measured total cyanide concentration is given in Table 4.3. Spike recoveries for added total cyanide were calculated for many of the samples. A summary of the various solution compositions and corresponding total cyanide concentrations are in this Table.

Table 4.3 Summary of Total Cyanide Concentration and the Associated Sample Treatment Procedures

Solution Matrix	Cyanide Added (ppb TCN as CN^-)	Meta-Arsenite Added (mg/l)	Free Chlorine Added (mg/l)	Measured Cyanide (ppb TCN as CN^-)	Spike Recovery (%)
Effluent Wastewater	0	0	0	<2	NA
DI Water	0	0	25	<2	NA
Effluent Wastewater	0	0	25	<2	NA
0.1 N NaOH	0	0	0	<2	NA
0.1 N NaOH	5	0	0	6.67	133.4
0.1 N NaOH	10	0	0	10.5	105
0.1 N NaOH	50	0	0	53.2	106.4
0.1 N NaOH	0	28	0	2.76	NA
0.1 N NaOH	0	56	0	2.81	NA
0.1 N NaOH	5	28	0	4.27	85
0.1 N NaOH	5	56	0	5.01	100
0.1 N NaOH	5	112	0	5.48	110
0.1 N NaOH	10	28	0	11.5	115
0.1 N NaOH	10	56	0	11.8	118
0.1 N NaOH	10	112	0	12.2	122
0.1 N NaOH	50	28	0	68.1	136
0.1 N NaOH	50	56	0	60.7	121
0.1 N NaOH	50	112	0	50.5	101
High pH Effluent Wastewater	0	28	0	3.56	NA
High pH Effluent Wastewater	0	56	0	2.84	NA
High pH Effluent Wastewater	5	56	0	10.8	139
High pH Effluent Wastewater	10	56	0	18.1	143
High pH Effluent Wastewater	50	56	0	65.7	124
Effluent Wastewater	0	28	25	2.6	NA
Effluent Wastewater	0	56	25	<2	NA
Effluent Wastewater	0	112	25	<2	NA

The practical quantitation limit for flow injection analysis of total cyanide is 2 ppb corresponding to a signal-noise ratio of three. The response for a 0.1 N sodium hydroxide solution containing 28 mg/l and 56 mg/l meta-arsenite were equivalent to 2.76 and 2.81 ppb respectively. These

values are close to the practical quantitation limit from which it can be inferred that there is no impact of the meta-arsenite on the total cyanide concentration in a high pH solution since the response of the 0.1 N sodium hydroxide was also below the detection limit.

The next group of samples tested the impact of meta-arsenite on a 0.1 N sodium hydroxide solution made in DI water, which was spiked with three different concentrations of total cyanide: 5, 10, 50 ppb total cyanide as cyanide ion. The meta-arsenite was added at three different concentrations for each total cyanide concentration. At each cyanide concentration, the meta-arsenite was dosed at three levels: 28, 56, and 112 mg/l. At 28 mg/l meta-arsenite, there is enough capacity to remove the highest typical chlorine doses used at municipal wastewater treatment. The other meta-arsenite doses were employed to see the impact of the quenching agent at extreme excess. The resulting total cyanide concentrations were determined and listed in Table 4.1. The spike recovery could then be determined by comparing the total cyanide concentration of the samples that had both cyanide and meta-arsenite added and the 0.1 N sodium hydroxide solution. The spike recovery was within the acceptable range of recoveries (75-125%) for all but one sample in this group. An explanation for the exception is unknown at this time. With this high corroborating evidence, the meta-arsenite does not impact the total cyanide concentration for sodium hydroxide solutions made with DI water that are spiked with cyanide.

The next group of experiments tested the impact of meta-arsenite on wastewater samples. Effluent wastewater samples were collected from the South Durham Wastewater treatment plant. This plant practices UV irradiation as the disinfection process; consequently, the wastewater was never chlorinated. Samples of wastewater were collected prior to the disinfection process to emulate the condition of the wastewater entering a chlorination process at other plants. Wastewater samples were spiked at three different concentrations of total cyanide (5, 10, and 50 ppb) and quenched with 56 mg/l meta-arsenite. These samples were compared to the wastewater sample to which 56 mg/l meta-arsenite was added but with no added cyanide to evaluate spike recoveries.

The total cyanide concentration for the 56 mg/l meta-arsenite treated wastewater samples spiked with 5, 10, 50 ppb total cyanide was 10.8, 18.1, and 65.7 ppb respectively. The spike recoveries are higher than expected (139, 143, and 124%). The spike recovery was evaluated by comparison to the wastewater sample at pH>12 with 56 mg/l of meta-arsenite added. This

indicates that the meta-arsenite did not negatively impact the total cyanide concentrations. An explanation for the higher than expected recoveries can then be attributed to the relatively low total cyanide concentration in the wastewater sample that was not spiked with cyanide (2.84 ppb) which is close to the practical quantification limit. There is more error associated with the low concentration part of the calibration curve. The unspiked, high pH, 56 mg/l meta-arsenite effluent wastewater sample cyanide level is not as certain as other samples that had resulted in higher cyanide concentrations. With this consideration, the addition of meta-arsenite to wastewater does not impact the total cyanide concentration.

The final step is to examine the effect of chlorination on total cyanide concentration when the residual chlorine is quenched with meta-arsenite. An aliquot of the effluent wastewater was chlorinated at 25 mg/l as Cl_2 and quenched at three different doses of meta-arsenite (28, 56, and 112 mg/l). There were no cyanide spikes on these samples. The impact of the meta-arsenite could be determined by analyzing the resulting cyanide concentrations and comparing these results to a wastewater sample that was chlorinated at the same dose but not quenched.

The resulting cyanide concentrations for the chlorinated wastewater which had 26, 56, and 112 mg/l meta-arsenite added were 2.6, <2, and <2 ppb respectively. This indicates that these samples had rather low cyanide concentrations, most of which were below detection. In addition, these samples can be compared to the chlorinated effluent sample at ambient pH cyanide concentration, which was not treated with meta-arsenite (<2 ppb). The meta-arsenite had no effect on the total cyanide concentration in the chlorinated wastewater. These samples were analyzed at ambient pH, so there is a chance of volatilization of the hydrogen cyanide. This is unlikely to be a cause of cyanide loss since the dominant form of cyanide is complex cyanide, which is soluble.

4.4 Minimum Detection Limit Determination

The minimum detection limit (MDL) was determined through analyzing seven replicates of a synthetic 2 ppb total cyanide solution. The average response and the standard deviation were calculated from the data for use of the following formula, given below, to calculate the MDL.

$$MDL = \frac{3.14 \times S \times Concentration_{calibrant}}{Height_{average}}$$

where S is the standard deviation of the response of the seven replicates of the 2 ppb calibrant. The response (peak height) was 1652.86 pA while the standard deviation was 69.53 pA. Using this data, the MDL was calculated to be 0.26 ppb as CN^-.

4.5 Wastewater Sample Nitrite Results and Discussion for Burlington, High Point (Round 1), and Greensboro

Nitrite analysis was performed on pre-chlorinated wastewater samples by ion chromatography (IC) for wastewater samples from the Burlington, High Point, Greensboro, and Winston-Salem utilities. The analysis for nitrite was performed on May 26, 1998. Each utility is composed of two separate plants that serve each community.

The sample holding time was longer than 48 hours for the analysis done for these wastewater samples, so it is possible that changes in the nitrite concentration occurred. The wastewater samples were stored at $4^{O}C$ until analysis. In addition, these samples did not have chloride removed. These samples were filtered before analysis to remove solids that would adversely effect the analytical instrumentation. Due to long run times and numerous samples, there were no duplicates or nitrite spikes of the samples.

Table 4.4 summarizes the nitrite concentration in these wastewater treatment plants. The South Burlington and the North Buffalo plants have the highest nitrite concentrations – 736 ppb and 2313 ppb respectively. All the other plants have much lower nitrite concentrations ranging from 66.4 ppb to 84.4 ppb which are more typical of a well operated activated sludge plant that is required to nitrify its waste (Metcalf and Eddy, 1991). Extrapolation of the calibration curve was used to determine the nitrite concentration in the North Buffalo wastewater sample.

Table 4.4 A Summary of the Nitrite Results for the Burlington, High Point, and Greensboro Utilities

Utility	Nitrite Concentration (ppb)
East Burlington	84.4
South Burlington	735.9
High Point Eastside	68.1
High Point Westside	76.2
T.K. Osborne (Greensboro)	66.4
North Buffalo (Greensboro)	2313.3

4.6 South Burlington Total Cyanide Results

Wastewater samples were collected from the South Burlington Wastewater Treatment plant on March 25, 1998. South Burlington is a nitrifying activated sludge plant whose total cyanide discharge permit is 5 ppb as CN^-. The plant utilizes chlorination as its disinfection process and is required to dechlorinate the wastewater with sulfur dioxide (SO_2) to remove any residual in the wastestream before its discharge to the receiving waters. The nitrite concentration of the pre-chlorination wastewater was 735.9 ppb, which is one of the highest values of the sampled wastewater treatment plants.

The sample collection procedure was the same as outlined in Chapter 3, although one of the stabilization procedures was not employed. The stabilization procedure involving the removal of both sulfide and nitrite simultaneously was not performed on these samples. In addition, the nitrite removal stabilization procedure was performed by adding a small amount of sulfamic acid crystals (~150 mg) to a 40 ml vial. The chlorine dose for the disinfection process at the time of sample collection was 2.5 mg/l.

Total cyanide concentrations for the South Burlington wastewater samples are summarized below in Figure 4.3 and Table 4.5. For the samples that were not treated for nitrite removal, there was a rather high apparent total cyanide concentration for the samples collected in the chlorine contact chamber. The total cyanide concentration for the sample that was treated only with meta-arsenite was 43.33 ppb and the sample that was both quenched and had sulfide removed had a total cyanide concentration of 49.06 ppb. Comparing these concentrations to the sample that was quenched and had nitrite removed, the latter exhibits a significantly lower total cyanide concentration. The total cyanide concentration in the sample collected in the chlorine contact chamber from which nitrite was removed at the time of sample collection was 6.14 ppb.

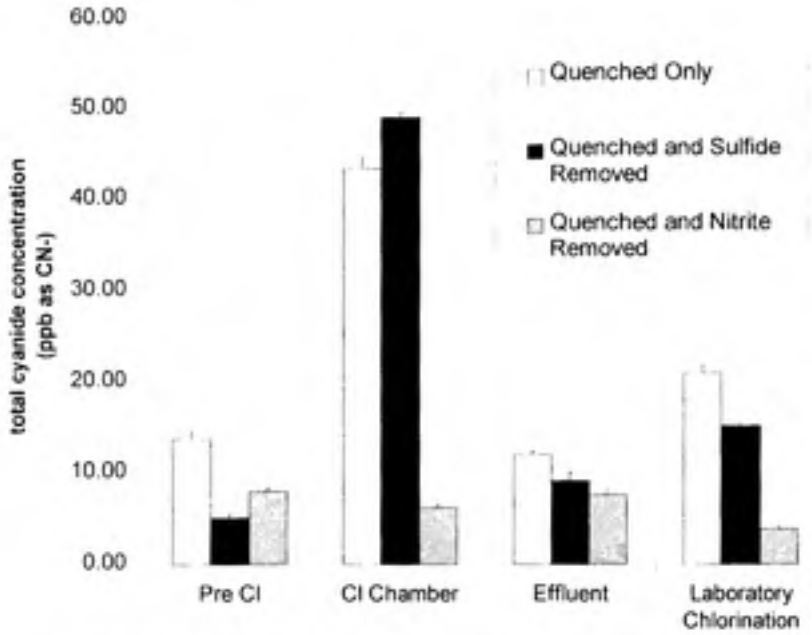

Figure 4.3 Total Cyanide Concentrations for the South Burlington Wastewater Treatment Plant as a Function of Sample Collection Point and Stabilization Procedure

Table 4.5 Total Cyanide Concentrations for South Burlington for all Sample Collection Points and Stabilization Procedures

	Concentration (ppb TCN as CN^-)	+/- (ppb TCN)
Chlorine Quenching Only		
Pre-chlorination	13.66	0.78
Mid Chlorine Chamber	43.33	1.22
Effluent	11.89	0.41
Laboratory Chlorination	20.93	0.80
Sulfide Removal		
Pre-chlorination	5.09	0.34
Mid Chlorine Chamber	49.06	0.49
Effluent	9.10	0.87
Laboratory Chlorination	15.06	0.27
Nitrite Removal		
Pre-chlorination	8.01	0.36
Mid Chlorine Chamber	6.14	0.32
Effluent	7.56	0.61
Laboratory Chlorination	3.82	0.29

Analysis of the total cyanide concentration for the pre-chlorination samples that had both sulfide and chlorine removed and the sample that had chlorine removed only reveals a much lower total cyanide, 5.09 and 13.66 respectively compared to the samples collected in the chlorine contact chamber. This demonstrates that the chlorination process may be involved in an apparent cyanide formation. In both the pre-chlorination and the mid chlorine chamber samples that were treated for nitrite, this same cyanide formation does not occur. The pre-chlorination sample that had nitrite removed had a nitrite concentration of 8.01 ppb. If chlorine were solely responsible for the cyanide formation, the cyanide concentration would be high no matter which stabilization procedures were employed. As long as the stabilization procedure did not destroy cyanide in the sample vial, all of the stabilization procedures should result in the same cyanide concentrations at each sample collection point. This is clearly not the case at this plant, so the cyanide formation is not occurring in the chlorine contact chambers.

The fact that the cyanide levels in samples from which nitrite was removed do not change significantly indicates that nitrite along with chlorine are responsible for this cyanide formation. The nitrite is then an artifact of the analytical method causing this cyanide formation. This is consistent with the findings of Carr et al, (1995) who found that nitrite caused a cyanide formation in the Standard Method 4500-CN test for total cyanide when coupled with a carbon source. The samples, which had nitrite removed, do not experience the same cyanide formation reaction as with the other samples. This leads to the conclusion that the cyanide formation is occurring after sample collection either while being held for analysis or in the sample analysis. The latter is the proposed hypothesis of Carr et al. (1995).

In order for the chlorine and the nitrite impact on the total cyanide concentration to be explained, the cyanide formation reaction is proposed to be a two step reaction. The chlorine must react with an unknown compound X to form another unknown compound Y in the chlorine contact chambers. This newly created unknown compound Y reacts with nitrite in the sample storage or analysis stage to form cyanide. It is also believed that this second reaction to form cyanide is a kinetically slow reaction, so there is no observable cyanide formation in the chlorine contact chambers. The hydraulic detention time for most of the chambers in the study was 15 minutes. This is not enough time for the second step of the cyanide formation reaction to occur; however, the several days of holding time in the sample vial is enough. This proposed reaction could then be completed downstream. The discharge of the nitrite and the reactive carbon would be diluted in the receiving waters. Any cyanide, which was formed downstream, would have the

propensity to volatilize from the surface waters due to the higher turbulence and ambient pH. The reaction is given below as an equation.

$$HOCl + X^{-} \rightarrow Y, \text{ in the chlorine contact chambers}$$
$$Y + NO_2^{-} \rightarrow CN^{-}, \text{ after the sample is collected}$$

Carr et al. (1995) found that ascorbic acid can act similar to a Y compound to form cyanide. Ascorbic acid is not formed by chlorination, but is often added after sample collection to remove any residual chlorine. This makes it available for this second stage of the cyanide formation reaction. Ascorbic acid is often used in excess to ensure complete removal of chlorine, so the unreacted portion could then be available for the cyanide formation reaction in the presence of nitrite. They made a DI water sample, which was spiked with nitrite and ascorbic acid. They did observe a positive cyanide concentration. It should be noted that their study was done with the Standard Method 4500-CN.

The removal of sulfide lowers the measured total cyanide concentration, compared to the samples that are only chlorine quenched, in two out of the three sample points. The exception is the mid chlorine contact chamber samples where an increase was observed. An explanation for this sample's higher cyanide concentration is unknown, but contamination of the filter used to removed the precipitated sulfides is possible.

In all but one stabilization procedure, the effluent samples have lower cyanide concentrations than the mid chamber samples that had the same stabilization procedures employed. The total cyanide concentration in the effluent samples for the quench only, sulfide removed, and nitrite removed are 11.89 ppb, 9.10 ppb, and 7.56 respectively. One might conclude that the lower levels relative to the mid chamber sample levels could be due to the volatilization of the cyanide in the chlorine contact chambers, but the impact of nitrite discussed earlier demonstrated that the cyanide formation is most likely happening after sample collection. One possible explanation of this is volatilization or oxidation in the chlorine contact chamber of a precursor material that leads to cyanide formation in the sample handling process.

The effluent concentration of total cyanide increased for the nitrite removed samples compared to the mid chamber sample. The mid chamber, nitrite removed sample has a much lower cyanide concentration than the other mid chamber samples. This indicates that this handling procedure

stops the process of cyanide formation. In fact, the change in cyanide concentration for the nitrite removed samples is almost totally explained by the standard deviations of the total cyanide concentrations of these two samples.

The laboratory chlorinations were carried out by chlorinating 500 ml of the pre-chlorination wastewater to 5.0 mg/l for 15 minutes. These were the doses and the detention time of the wastewater at the treatment plant at the time of sample collection. Theoretically, the laboratory chlorinations should correspond to the effluent values of the same stabilization procedure. In two out of the three stabilization procedures, the cyanide concentration was lower in the effluent sample compared to the laboratory chlorination. The explanation of this is an inadvertent chlorine overdose done in the laboratory due to inaccurate information obtained in the field.

The removal of nitrite in the laboratory chlorination lowered the total cyanide concentration compared to the plant effluent sample. The expected result would be that there would be no change in the total cyanide concentration due to the nitrite removing. The fact that this concentration is lower can then be attributed to the fact that the laboratory chlorinations were done two days after the sample collection and the wastewater underwent chemical composition changes that increased the nitrite concentration while being held for the chlorination experiment.

4.7 East Burlington Total Cyanide Results

Wastewater samples for the East Burlington Wastewater Treatment Plant were collected on April 2, 1998. The East Burlington Wastewater treatment plant is a nitrifying activated sludge treatment plant that practices chlorination as the disinfection process. This plant also utilizes tertiary sand filtration to enhance the effluent quality. The sand filters are situated between the chlorine addition point and the chlorine contact chamber. The plant is also required to remove any chlorine residual before discharge into the receiving waters. This is accomplished by the addition of sulfur dioxide (SO_2) to the wastestream. Analysis of the preserved, pre-chlorination wastewater revealed a nitrite concentration of 84.4 ppb.

Samples collected underwent the sample stabilization procedure as outlined in Chapter 3 with one exception. The nitrite removal step was performed by the addition of ~150 mg of sulfamic acid crystals to the 40 ml vial. This sample trip also marks the first time that the nitrite was removed simultaneously with the sulfide.

Total cyanide results of this plant did not demonstrate the significant cyanide formation as seen with South Burlington. With the nitrite concentration of the East Burlington wastewater (84.4 ppb) much lower than the South Burlington wastewater (735.9 ppb), the effect of nitrite removal cannot be as significant as with high nitrite wastewaters. Table 4.6 and Figure 4.4 summarize the total cyanide concentrations as a function sample collection point and stabilization procedure. The laboratory chlorinations total cyanide concentrations were excluded in the Figure 4.5 since these values were so much greater than the other values seen in collected wastewater samples. This made the trends easier to analyze in the graphical representation of the cyanide concentrations.

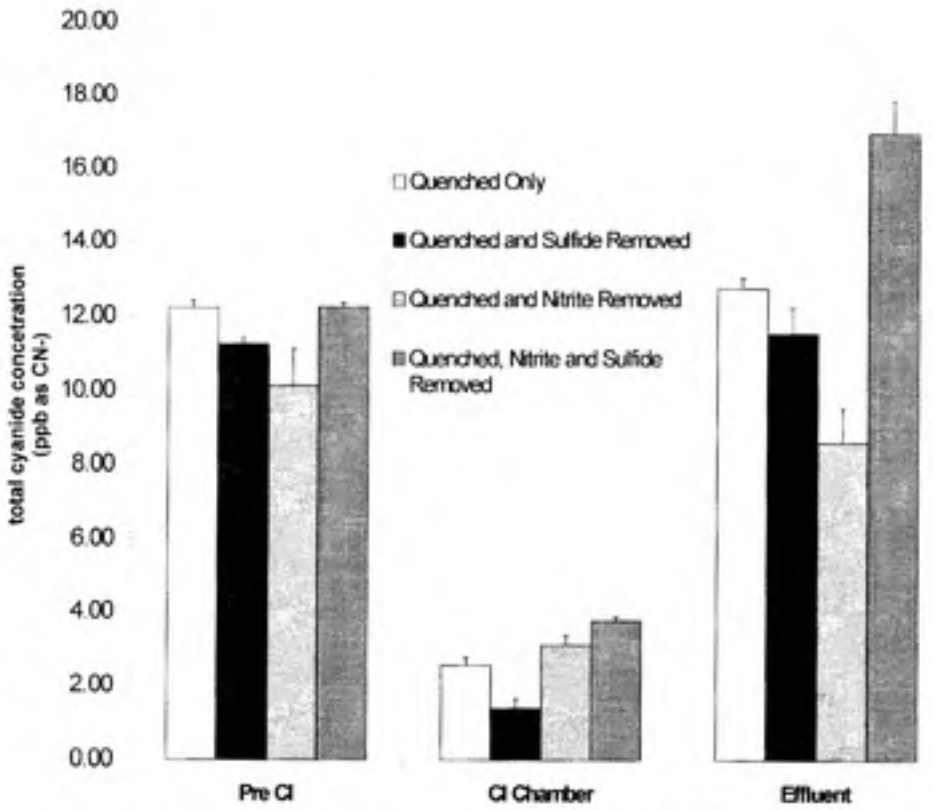

Figure 4.4 Total Cyanide Concentrations for the East Burlington Wastewater Treatment Plant as a Function of Sample Collection Point and Stabilization Procedure

Table 4.6 Total Cyanide Concentration for the East Burlington Wastewater as a Function of Sample Collection Point and Stabilization Procedure

	Concentration (ppb TCN as CN^-)	+/- (ppb TCN)
Quench Only		
Pre-chlorination	12.23	0.22
Mid Chlorine Chamber	2.56	0.20
Effluent	12.74	0.28
Laboratory Chlorination	60.11	0.65
Sulfide Removed		
Pre-chlorination	11.27	0.15
Mid Chlorine Chamber	1.40 bdl	0.25
Effluent	11.53	0.69
Laboratory Chlorination	21.76	0.30
Nitrite Removed		
Pre-chlorination	10.15	0.98
Mid Chlorine Chamber	3.11	0.26
Effluent	8.59	0.93
Laboratory Chlorination	7.53	0.43
Sulfide and Nitrite Removed		
Pre-chlorination	12.25	0.12
Mid Chlorine Chamber	3.77	0.10
Effluent	16.92	0.89
Laboratory Chlorination	5.31	0.36

Legend: bdl – below detection limit

Comparison of the mid chlorine contact chamber samples to the other sample points (pre-chlorination and effluent) demonstrates a significantly lower total cyanide concentration. In fact, the "sulfide removed sample" collected in the chlorine contact chamber indicates a total cyanide concentration below the practical quantitation limit of 2 ppb. The other mid chamber samples were close to this quantitation limit.

The pre-chlorination samples have approximately the same total cyanide concentration as the effluent samples. The average of these samples is approximately 11 ppb for the pre-chlorination

and effluent samples. The mid chamber samples have an average total cyanide concentration of approximately 3 ppb. An explanation of the decrease in the total cyanide concentration in the chlorine contact chamber samples is unknown.

Even at the low nitrite concentrations of this wastewater, there is still a reduction of total cyanide if the sample is treated for nitrite. Comparison of the quench only samples to the nitrite removed samples reveals a decrease in cyanide concentrations for all sample points except the chlorine contact chamber samples. An explanation of this discrepancy is that the cyanide concentration difference for the nitrite removed sample and the quench only sample collected in the chlorine contact chamber is not statistically different by comparison of the standard deviations of these concentrations. The cyanide concentration in the pre-chlorination sample point decreased from 12.33 ppb in the quench only sample to 10.15 ppb for the nitrite removed sample. The same comparison to the effluent samples found a cyanide concentration reduction from 12.74 ppb for the quench only sample to 8.59 ppb for the nitrite removed sample. In the laboratory chlorination, there was a dramatic cyanide decrease from the quench only sample (60.11 ppb) to the nitrite removed sample (7.53 ppb).

The removal of sulfide lowered the total cyanide concentration at every sample point. The average cyanide decrease due to sulfide removal was approximately 1 ppb for all samples except the laboratory chlorination where the cyanide levels decreased from 60.11 ppb to 21.76 ppb.

The laboratory chlorination total cyanide concentrations are significantly greater than the other samples. The wastewater used for the laboratory chlorination was only refrigerated until analysis and chlorinated four days after sample collection. Wastewater is not a stable matrix for cyanide and nitrite, so the possibility of the wastewater characteristics changing while being held exists. The sample was refrigerated until chlorination, and immediately after chlorination, the samples were preserved as described in Chapter 3. It is possible for the sample to contain nitrifying bacteria that changed the nitrite concentration.

4.8 High Point Sample Results (Round 1)

Two wastewater treatment plants serve the community of High Point, North Carolina designated as the Eastside and Westside plant. The High Point plants are nitrifying activated sludge plant that uses chlorine as the disinfection agent. To further enhance the quality of the effluent wastewater, both plants practice tertiary filtration. Wastewater samples were collected on April

13, 1998 for both plants. The chlorine dose for the Eastside and Westside plant was 2.82 mg/l as Cl_2 and 2.46 mg/l as Cl_2. The cyanide discharge permit for these plants is 5 ppb.

The samples were collected and stabilized in the same manner as described in Chapter 3 with a few exceptions. The removal of nitrite was performed by adding ~150 mg of sulfamic acid to the 40 ml vial.

The effect of nitrite was so dramatic in the previous analyzed South Burlington sample that more investigation into the effect of sulfamic acid on total cyanide analysis was pursued for the High Point samples. Standard Method 4500-CN requires the addition of sulfamic acid be immediately before analysis. In the previous sampling of the Burlington utility, the addition of sulfamic acid was done at the time of collection. In these current samples, the addition of sulfamic acid was done at the time of collection (at source) and before just analysis to determine definitively whether the cyanide formation reaction was occurring in the sample vial while being held for analysis or in the acid digester of the analytical instrumentation.

Each plant for this utility collected effluent wastewater samples at the same time as UNC to comply with the discharge permit. These samples were tested for total cyanide according to the Standard Methods 4500-CN method by a contract laboratory and shown to have total cyanide levels of 10 ppb for both plants.

4.8.1 High Point Eastside Total Cyanide Results

Analysis of the pre-chlorination wastewater revealed a low nitrite concentration (68.1 ppb). This would indicate that there should not be a drastic cyanide formation as seen with higher nitrite concentrations. Indeed, these are the observed results. Table 4.7 and Figure 4.5 summarize the cyanide concentrations for the various sample points and stabilization procedure.

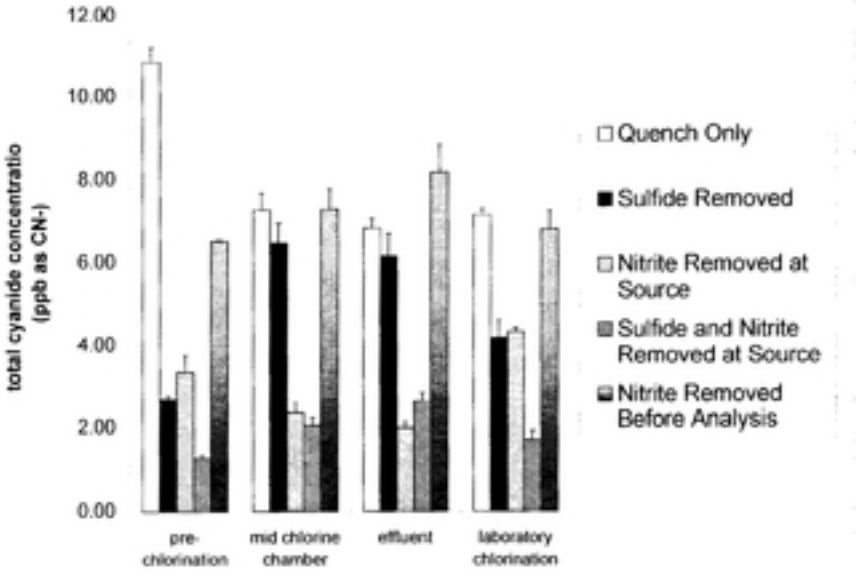

Figure 4.5 Total Cyanide Concentrations for High Point Eastside as a Function of Stabilization Procedure and Sample Collection Point

Table 4.7 Total Cyanide Concentrations for the High Point Eastside Wastewater Treatment Plant as a Function of Sample Collection Point and Stabilization Procedure

	Concentration (ppb as CN^-)	+/- (ppb TCN)
Quench Only		
pre-chlorination	10.84	0.36
mid chlorine chamber	7.27	0.40
effluent	6.82	0.23
laboratory chlorination	7.13	0.14
Sulfide Removed		
pre-chlorination	2.65	0.12
mid chlorine chamber	6.47	0.47
effluent	6.15	0.54
laboratory chlorination	4.17	0.42
Nitrite Removed at Source		
pre-chlorination	3.35	0.40
mid chlorine chamber	2.36	0.20
effluent	bdl	0.14
laboratory chlorination	4.32	0.10
Sulfide and Nitrite Removed at Source		
pre-chlorination	bdl	0.06
mid chlorine chamber	2.05	0.19
effluent	2.63	0.22
laboratory chlorination	bdl	0.21
Sulfide and Nitrite Removed Before Analysis		
mid chlorine chamber	3.72	NA
Nitrite Removed Before Analysis		
pre-chlorination	6.52	0.02
mid chlorine chamber	7.28	0.48
effluent	8.17	0.67
laboratory chlorination	6.79	0.44

There appears to be no statistical or logical trend of cyanide concentrations through the disinfection process. The cyanide concentrations have no overall pattern of one sample point having statistically different cyanide concentrations. The quench only samples have approximately the same cyanide levels for the chlorine contact chamber, effluent, and laboratory chlorination samples (~7 ppb) while the pre-chlorination sample is much greater at 10.84 ppb. The sulfide removed samples have the greatest cyanide concentrations for the chlorine contact chamber samples and the effluent sample (~6 ppb) while the pre-chlorination and the laboratory chlorination have a lower cyanide concentration of ~3.5 ppb. The cyanide concentration for the samples that had nitrite removed at source does not indicate any logical trend. These values are an average of ~3 ppb. The sulfide and nitrite removed samples have a cyanide concentration close to the quantitation limit of this methodology (2 ppb). The samples that had nitrite removed immediately before analysis had an average cyanide concentration of ~7 ppb.

The removal of sulfide lowered the cyanide levels in all sample points when compared to the quench only sample. The pre-chlorination sample cyanide concentration decreased from 10.84 ppb in the quench only sample to 2.65 ppb. The chlorine contact chamber did show a decrease in cyanide concentrations when sulfide was removed to that when the sample was only quenched. This decrease is not statistically significant though. This is also the case for the effluent samples. The laboratory chlorination experienced a statistically significant decrease in cyanide concentrations when sulfide is removed. The total cyanide concentrations decreased from 7.13 ppb in the quench only sample to 4.17 ppb in the sulfide removed. This data indicate that the removal of sulfide can lower the cyanide levels in wastewater. This leads to the conclusion that the wastewater contains low level sulfide concentrations that need to be removed from the wastewater before cyanide analysis.

The removal of nitrite at source also demonstrated a significant decrease in cyanide concentrations for all sample points when compared to the quench only samples. This difference is statistically different for each sample point. The cyanide concentration decreased from 10.84 ppb to 3.35 ppb for the pre-chlorination samples. The mid chamber samples decreased from 7.27 ppb to 2.36 ppb while the effluent sample decreased from 6.82 ppb to below detection limit of 2 ppb. A decrease from 7.13 ppb to 4.32 ppb was observed in the laboratory chlorination. This is further proof that nitrite is involved with a cyanide formation reaction.

An interesting observation is found when the comparison of the samples that have nitrite removed at source as opposed to the samples that have nitrite removed immediately before analysis. Standard Method 4500-CN calls for the sulfamic acid to be added immediately before analysis. This will result in the removal of the nitrite before analysis. The theory behind this is that the nitrite is converted into nitrous acid (HNO_2) in the acid digester of the Standard Method apparatus (Carr et al., 1995). The nitrous acid, a known strong redox reagent, reacts with a carbon source to form cyanide in the digestion process. Because this cyanide formation occurs in the digester, the removal of nitrite should be done before analysis. The samples in which nitrite is removed just before analysis most closely correspond to the Standard Methods procedure.

The observed results indicate that the cyanide concentrations are much greater in the samples that have nitrite removed immediately before analysis when compared to the samples that have nitrite removed at source. At every sample point, the cyanide concentration is significantly lower for the samples that have nitrite removed at source. Addition of the sulfamic acid at the time of sample collection for the pre-chlorination samples reduced the cyanide concentration from 6.52 ppb to 3.35 ppb when compared to the samples that had the sulfamic acid added immediately before analysis. The same comparison done for the chlorine contact chamber samples show a cyanide concentration decrease from 7.28 ppb to 2.36 ppb. The decrease in cyanide levels was from 8.17 ppb to 1.98 ppb for the effluent samples. The laboratory chlorination total cyanide concentration decreased from 6.79 ppb to 4.32 ppb when comparing the time of sulfamic acid addition.

If the cyanide formation reaction were truly occurring in the digester, the cyanide concentrations should be the same no matter when the nitrite was removed; however, there is a dramatic difference in cyanide concentration for these samples. The only difference in these samples is the time of the nitrite removal. For the High Point chlorinated samples, it can be concluded that the cyanide formation reaction may be occurring in the sample vial containing nitrite while being held for analysis. This is not in concurrence with the literature, which states that the cyanide formation reaction occurs in the acid digester of the Standard Method apparatus.

Further proof of this hypothesis is revealed when the samples that had the nitrite removed before analysis are compared to the quench only samples. Comparing these stabilization procedures at the same sample collection point, there is an observed correspondence of the cyanide

concentrations for all sample collection points except for the pre-chlorination sample point. The fact that these samples have approximately the same cyanide concentration indicates that the sulfamic acid is not removing the nitrite interference for the cyanide analysis. This observation is in agreement with the hypothesis of the cyanide formation reaction occurring in the sample vial while being held for analysis.

The pre-chlorination quench only sample is unrealistically high. The total cyanide concentration could be lowered due to sulfide removal , but the sample has not been subjected to chlorination. According to the proposed hypothesis, there could be no lowering the total cyanide concentration due to nitrite removal. Therefore, the cyanide formation reaction could not occur unless there is influent reactive carbon that form cyanide in the presence of nitrite to the chlorine contact chamber.

The removal of sulfide and nitrite concurrently lowers the cyanide concentration more than any other sample stabilization procedure. All of the values are close to the practical detection limit of the instrument. In fact, two of the sample collection points are below this detection limit – pre-chlorination and laboratory chlorination. Presumably, this is due to the removal of sulfide and nitrite interferences, which contribute to elevated cyanide concentrations. It should be noted that the nitrite removal was done at the time of sample collection; however, samples that had simultaneous sulfide and nitrite removal performed at the time of collection were analyzed. The cyanide concentration in this sample was greater than the sample that had sulfide and nitrite removed at source – 3.72 ppb versus 2.63 ppb respectively. This comparison indicates that the removal of nitrite should be done at the time collection, since this sample indicates cyanide formation is occurring in the sample vial before analysis.

4.8.2. High Point Westside Total Cyanide Results

Analysis for the Westside pre-chlorination wastewater revealed a nitrite concentration of 76.2 ppb. This nitrite concentration is expected not to cause drastic cyanide formation as seen in the South Burlington wastewater, but there exists the possibility of a smaller amount of cyanide formation due to the lower nitrite concentration. This was the observation at the High Point Eastside treatment plant. Table 4.8 and Figure 4.6 summarize the cyanide results for the given stabilization procedure and sample collection points.

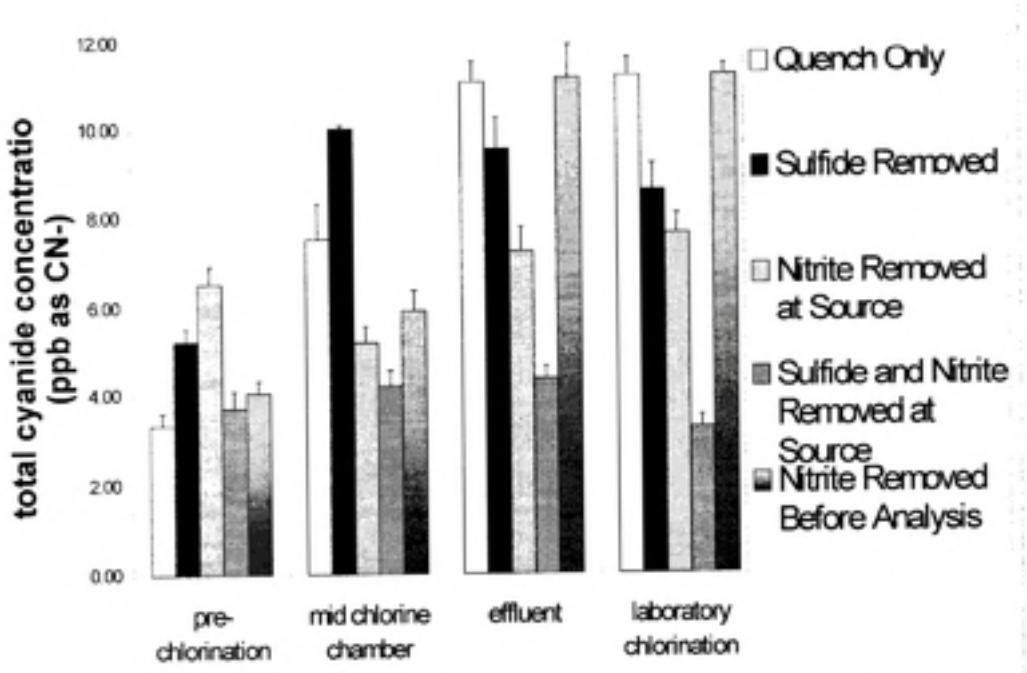

Figure 4.6 Total Cyanide Concentrations for the High Point Westside Wastewater Treatment Plant as a Function of Sample Collection Point and Stabilization Procedure

Table 4.8 Total Cyanide Concentrations for the High Point Westside Wastewater Treatment Plant as a Function of Sample Collection Point and Stabilization Procedure

	Concentration (ppb TCN)	+/- (ppb TCN)
Quench Only		
pre-chlorination	3.34	0.26
mid chlorine chamber	7.51	0.79
effluent	11.01	0.49
laboratory chlorination	11.15	0.42
Sulfide Removed		
pre-chlorination	5.22	0.29
mid chlorine chamber	9.99	0.07
effluent	9.52	0.70
laboratory chlorination	8.58	0.59
Nitrite Removed at Source		
pre-chlorination	6.53	0.41
mid chlorine chamber	5.18	0.37
effluent	7.22	0.54
laboratory chlorination	7.61	0.42
Sulfide and Nitrite Removed at Source		
pre-chlorination	3.71	0.38
mid chlorine chamber	4.19	0.35
effluent	4.35	0.27
laboratory chlorination	3.24	0.25
Sulfide and Nitrite Removed Before Analysis		
mid chlorine chamber	7.39	NA
Nitrite Removed Before Analysis		
pre-chlorination	4.03	0.28
mid chlorine chamber	5.90	0.46
effluent	11.11	0.79
laboratory chlorination	11.16	0.26

The cyanide concentration increased through the disinfection process for the quench only samples. The pre-chlorination sample had the lowest cyanide concentration (3.34 ppb) of these

samples. For the quench only samples, the chlorine contact chamber, effluent, and laboratory chlorination sample had cyanide concentrations of 7.51 ppb, 11.01 ppb, and 11.15 ppb. This increase could be attributed to the chlorination process coupled with the low concentration of nitrite to form cyanide. The fact that the effluent sample has a greater cyanide level than the chlorine contact chamber sample may be due to an incomplete reaction of the chlorination step of this cyanide formation reaction in the latter sample.

The cyanide concentration for the sulfide removed sample in the chlorine contact chamber (9.99 ppb) was greater than the sulfide removed sample collected before the point of chlorination (5.22 ppb), a trend which is consistent with the quench only samples. Removal of sulfide raises the cyanide levels for the pre-chlorination and mid chamber sample points while the cyanide concentration is lowered for the effluent sample point and the laboratory chlorination when sulfide is removed. There is no definitive evidence if sulfide is present in these samples.

Comparison of the stabilization procedure did reveal significant trends. The samples that had sulfide and nitrite removed concurrently had lower cyanide concentrations when compared to any other stabilization procedure. Removing nitrite at source samples had lower cyanide concentration than the quench only samples with the only exception being the pre-chlorination samples. This trend was seen in the High Point Eastside plant leading to the conclusion that nitrite must be removed to accurately portray the cyanide concentrations in wastewater samples, otherwise potential cyanide could be generated in the sample after collection.

Comparison of the nitrite removed at source samples to the nitrite removed before analysis revealed a significant cyanide concentration decrease for the chlorinated samples. The pre-chlorination sample did not show this trend which indicates that the chlorination changed the characteristics of the organics in the wastewater to be amenable to cyanide formation in the presence of nitrite.

Comparison of the chlorine contact chamber sample that had concurrent sulfide and nitrite removed at source to the chlorine contact chamber sample that had concurrent sulfide removed and nitrite removed before analysis demonstrated the expected increase in cyanide concentration. The cyanide concentration of the former is 4.19 ppb while the latter has a cyanide concentration of 7.39 ppb. These samples indicate that the cyanide formation is occurring in the sample vial; thus, removal of nitrite is appropriate at the time of sample collection. This effect was not seen

as clearly in the samples that tested the time of nitrite removal with the concurrent removal of sulfide.

4.9 Greensboro Sample Results

Two wastewater treatment plants (T.K. Osborne and North Buffalo) service the city of Greensboro, North Carolina. These plants are activated sludge plants that nitrify the wastewater to comply with the discharge permits. Both plants use chlorination as the disinfection process. The chlorine dose for both plants was 5.0 mg/l at the time of sample collection. Wastewater samples were collected on April 24, 1998. The discharge permit for cyanide is 10 ppb at both plants. The samples were collected simultaneously by the plant to comply with the discharge permit and were analyzed by contract laboratories indicating a total cyanide concentration of less than 5 ppb using Standard Method 4500-CN.

Samples were collected in the same manner as described in Chapter 3 with the only exception being that the nitrite was removed with the addition of ~150 mg of sulfamic acid directly to the sample vial for the nitrite removal at source stabilization procedures.

Analysis of the nitrite concentration in the pre-chlorination wastewater revealed low nitrite concentrations in the T.K. Osborne plant (66.4 ppb), but an extremely high nitrite concentration was observed in the North Buffalo plant (2313.3 ppb). The laboratory chlorinations were dosed at 5 mg/l.

4.9.1 North Buffalo Total Cyanide Concentrations

Nitrite analysis of the pre-chlorination wastewater determined the nitrite concentration to be extremely high (2.3 mg/l). Figure 4.7 and Table 4.9 outline the total cyanide concentration in the North Buffalo Wastewater as a function of sample collection point and stabilization procedure.

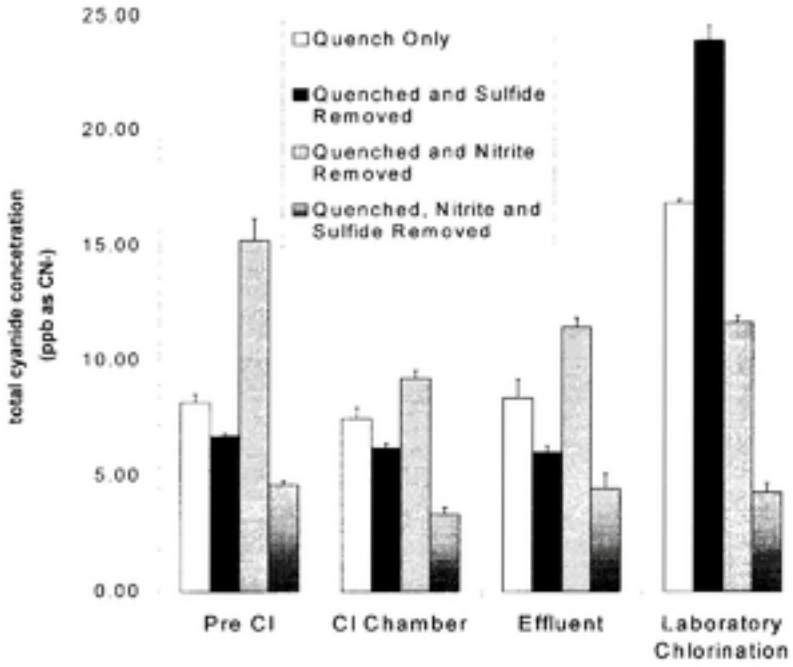

Figure 4.7 Total Cyanide Concentrations for Greensboro North Buffalo Wastewater Samples as a Function of Sample Collection Point and Stabilization Procedure

Table 4.9 Total Cyanide Concentration for the Greensboro North Buffalo Wastewater Samples as a Function of Sample Collection Point and Stabilization Procedure

	Total Cyanide Concentration (ppb as CN^-)	+/- (ppb TCN)
Quench Only		
pre-chlorination	8.14	0.35
mid chlorine chamber	7.45	0.45
effluent	8.30	0.80
laboratory chlorination	16.82	0.13
Sulfide Removed		
pre-chlorination	6.70	0.12
mid chlorine chamber	6.18	0.20
effluent	5.98	0.29
laboratory chlorination	23.92	0.62
Nitrite Removed at Source		
pre-chlorination	15.23	0.95
mid chlorine chamber	9.16	0.36
effluent	11.41	0.42
laboratory chlorination	11.60	0.28
Sulfide and Nitrite Removed at Source		
pre-chlorination	4.62	0.16
mid chlorine chamber	3.34	0.28
effluent	4.44	0.62
laboratory chlorination	4.29	0.39

In spite of the apparent high nitrite levels, there was not a dramatic cyanide formation associated with the chlorination of wastewater. The observed cyanide concentration patterns are those typically seen at plants that have low nitrite concentrations. One possible explanation is the nitrite concentration was not as great as the IC analysis indicated. The retention time for the peak was consistent with the other wastewater samples, but there could have been interference of another anion in the analysis. Another explanation is the absence of carbon containing precursor materials that are needed in the cyanide formation reaction. Characterization of such reactive carbon material was beyond the scope of this project, so identification of these compounds was not done.

Analysis of the laboratory chlorinated sample revealed higher cyanide concentrations when compared to the effluent samples. Theoretically, the laboratory chlorination should follow the same trends as the effluent samples; however, the effluent quench only (8.30 ppb) and the sulfide removed (5.89 ppb) were lower than the laboratory chlorination quench only sample (16.82 ppb). When nitrite was removed either simultaneously with sulfide removal or alone, the cyanide concentration corresponded extremely well. Both samples had a cyanide concentration of ~11.5 ppb for nitrite removed at source and ~4.3 ppb for sulfide and nitrite removed simultaneously. Since the samples chlorinated in the lab had been held for several days, it is likely that the wastewater sample had changes occur in the nitrite content. This caused the laboratory chlorination samples, which have no considerations for the nitrite interference, to have different cyanide concentrations than in the effluent samples which underwent the same stabilization procedure. The laboratory chlorination samples that had sulfamic acid added to remove the nitrite interference demonstrated the same cyanide levels as the effluent samples that had the same stabilization procedures performed.

The samples collected at different points in the plant have approximately the same cyanide concentration keeping the stabilization procedure constant. The removal of sulfide lowered the average cyanide concentration to ~6 ppb indicating that there is a presence of a small amount of sulfide contributing to elevated cyanide concentration.

When nitrite was removed in the pre-chlorination sample, the cyanide concentration increased to an average of ~11.5 ppb compared to the quench only samples (~8 ppb). This is not expected and such an increase is not explainable. The removal of nitrite in the laboratory chlorination did not increase the cyanide concentration. This procedure is done under more controlled conditions, so this results is likely to be more reliable and indicates the nitrite is a source of potential cyanide when left in a quenched wastewater sample.

The simultaneous removal of nitrite and sulfide had the lowest cyanide concentrations when compared to any of the other stabilization procedure. The average cyanide concentration for this stabilization procedure was ~4 ppb. The likelihood, therefore, is that both nitrite and sulfide act to produce a positive interference for total cyanide analysis during sample collection and analysis. To obtain a true measure of the cyanide content in the wastewater at the time of collection, these nitrite and sulfide removing stabilization procedures must be employed.

4.9.2 T.K. Osborne Total Cyanide Concentrations

Analysis of the nitrite concentration in the Osborne pre-chlorination wastewater sample revealed a low nitrite concentration. The expected cyanide formation resulting from the presence of nitrite should be small if present at all. Figure 4.8 and Table 4.10 summarize the total cyanide concentrations for the Osborne plant.

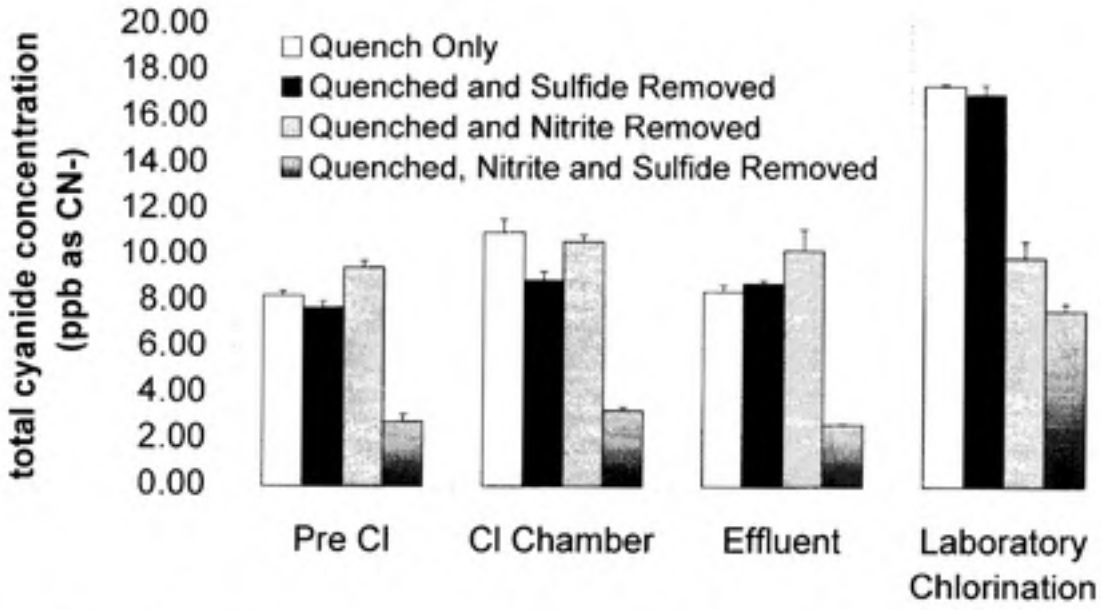

Figure 4.8 Total Cyanide Concentrations for the Osborne Wastewater Samples as a Function of Sample Collection Point and Stabilization Procedure

Table 4.10 Total Cyanide Concentrations for the Greensboro T.K. Osborne Wastewater Treatment Plant Wastewater as a Function of Sample Collection Point and Stabilization Procedure

	Total Cyanide Concentration (ppb as CN^-)	+/- (ppb TCN)
Quench Only		
pre-chlorination	8.26	0.19
mid chlorine chamber	10.99	0.59
effluent	8.41	0.29
laboratory chlorination	17.31	0.07
Sulfide Removed		
pre-chlorination	7.73	0.28
mid chlorine chamber	8.90	0.40
effluent	8.76	0.14
laboratory chlorination	16.94	0.43
Nitrite Removed at Source		
pre-chlorination	9.46	0.30
mid chlorine chamber	10.60	0.26
effluent	10.18	0.92
laboratory chlorination	9.87	0.72
Sulfide and Nitrite Removed at Source		
pre-chlorination	2.77	0.32
mid chlorine chamber	3.26	0.16
effluent	2.66	0.03
laboratory chlorination	7.58	0.32

The cyanide concentration in the plant samples did not significantly change throughout the chlorination process for any of the stabilization procedure. The quench only, sulfide removed, and the nitrite removed samples all have an average cyanide concentration of ~9 ppb. The fact that the stabilization procedures have the same cyanide concentration indicates that there was no cyanide formation potential in this wastewater. The cyanide measured in these samples is then associated with influent sources of cyanide to the treatment plant.

When sulfide and nitrite are removed concurrently, the total cyanide concentration decreases to an average of ~3 ppb. This is surprising since the stabilization procedure individually did not decrease the cyanide concentrations. The observed total decrease in the simultaneous removal of nitrite and sulfide should be equal to the sum of the cyanide removals from each individual stabilization processes. This is clearly not the case, so other explanations are needed and are unknown at this time.

The laboratory chlorination had significantly higher cyanide concentrations for the quench only (17.31 ppb) and sulfide removed sample (16.94 ppb). When the nitrite was removed from the laboratory chlorination, the cyanide concentration (9.87 ppb) decreased significantly to be at the same level as the effluent sample that had nitrite removed (10.18 ppb). This indicates a nitrite interference was removed in this sample to be consistent with the effluent sample, thus implying a nitrite content change in the laboratory chlorination wastewater. The simultaneous removal of nitrite and sulfide further reduced the cyanide concentration (7.58 ppb) from the sample that was only nitrite removed (9.87 ppb). The reduction can be attributed to sulfide removal in this sample. The removal of sulfide was not significantly shown in the sample that only had sulfide removal when compared to the sample that was only quenched, but this sulfide interference was shown in the concurrent removal of sulfide and nitrite samples.

4.10 Winston-Salem Sample Results

Two plants, designated as Muddy Creek and Archie Elledge, serve the city of Winston-Salem, North Carolina. Both are activated sludge plants that nitrify the wastewater to comply with the discharge permits. The disinfection process is performed through the chlorination of the wastewater at both plants. Wastewater samples were collected on June 30, 1998. The Muddy Creek treatment plant has no discharge limits on cyanide, but the discharge limit for the Archie Elledge plant is 6.6 ppb. An interesting qualification was added to the cyanide discharge permit. Through an extensive study of the reliability of the Standard Method 4500-CN for this plant, enough evidence was presented that the detection limit of the methodology was set at 20 ppb. Any result that is less than 20 ppb is reported as below detection, so violations of the cyanide discharge permit are rare at this plant.

4.10.1 Pre-Chlorination Wastewater Nitrite Analysis

The pre-chlorination wastewater from both plant was analyzed for nitrite by ion chromatography within a week of sample collection. These samples were analyzed by the procedure given in Chapter 3.

The nitrite results for the pre-chlorination wastewater revealed an extremely high nitrite concentration for the Muddy Creek wastewater sample (3130.55 ppb), while Archie Elledge had no detectable nitrite concentration in the pre-chlorination wastewater. The Muddy creek sample had a nitrite concentration greater than any other wastewater sample.

Quality control of the nitrite analysis on both wastewater samples was performed involving a 50 ppb spike of wastewater. The nitrite spike was added to the wastewater sample before analysis. The analysis of the nitrite spike recovery can verify the validity of the analytical procedures and aid the identification of the component in the chromatogram. The spike recoveries for the Muddy Creek and Archie Elledge wastewater sample were 75.02% and 92.64% respectively. This is well within accepted standards of recoveries; thus, the validity of the analytical procedure is assured. A table summarizing the results of the nitrite analysis is given below as Table 4.11.

The next group of samples was the same nitrite spiked wastewater samples that had sulfamic acid added to them to remove the nitrite. This was done to prove that the sulfamic acid does remove nitrite in wastewater. It is well known that sulfamic acid removes nitrite in DI water samples and was believed to remove nitrite in wastewater. This experiment showed without doubt that the sulfamic acid removed all nitrite in wastewater.

Table 4.11 A Summary of the Nitrite Concentrations for the Winston-Salem Wastewater Samples and the Subsequent Spikes and Treatments

Name	Nitrite Concentration (ppb as nitrite)	Spike Recovery (%)
Archie Elledge	3130.55	
Archie Elledge spiked with 50 ppb nitrite	3168.06	75.02
Archie Eddy with Sulfamic Acid	bdl	
Muddy Creek	bdl	
Muddy Creek spiked with 50 ppb nitrite	46.32	92.64
Muddy Creek with Sulfamic Acid	bdl	

PQL – 40 ppb

4.10.2 Total Cyanide Results for Winston-Salem

The standard stabilization procedures were employed for this group of wastewater samples – Chlorine Quenching, Sulfide Removal, and Nitrite Removal at Source, and Simultaneous Removal of Nitrite and Sulfide. To test the nitrite impact on total cyanide and further validate the hypothesis that the cyanide formation is occurring in the sample vial prior to analysis, nitrite removal was also done just before analysis.

In addition to the standard set of sample collection points and laboratory chlorination, a nitrite spiked laboratory chlorination was performed to further test the nitrite interference. The spike level was chosen at 700 ppb since that was a nitrite concentration proven to cause significant cyanide formation in the South Burlington Wastewater Treatment Plant.

4.10.2.1 Total Cyanide Results for Muddy Creek

Analysis of the nitrite concentration failed to detect any nitrite in the wastewater samples; however, there could still be some cyanide formation associated with nitrite if the proper precursor materials are present since the quantitation limit of the nitrite analytical method is 40 ppb. Figure 4.9 and Table 4.12 summarize the total cyanide concentration as a function of sample collection point and stabilization procedure.

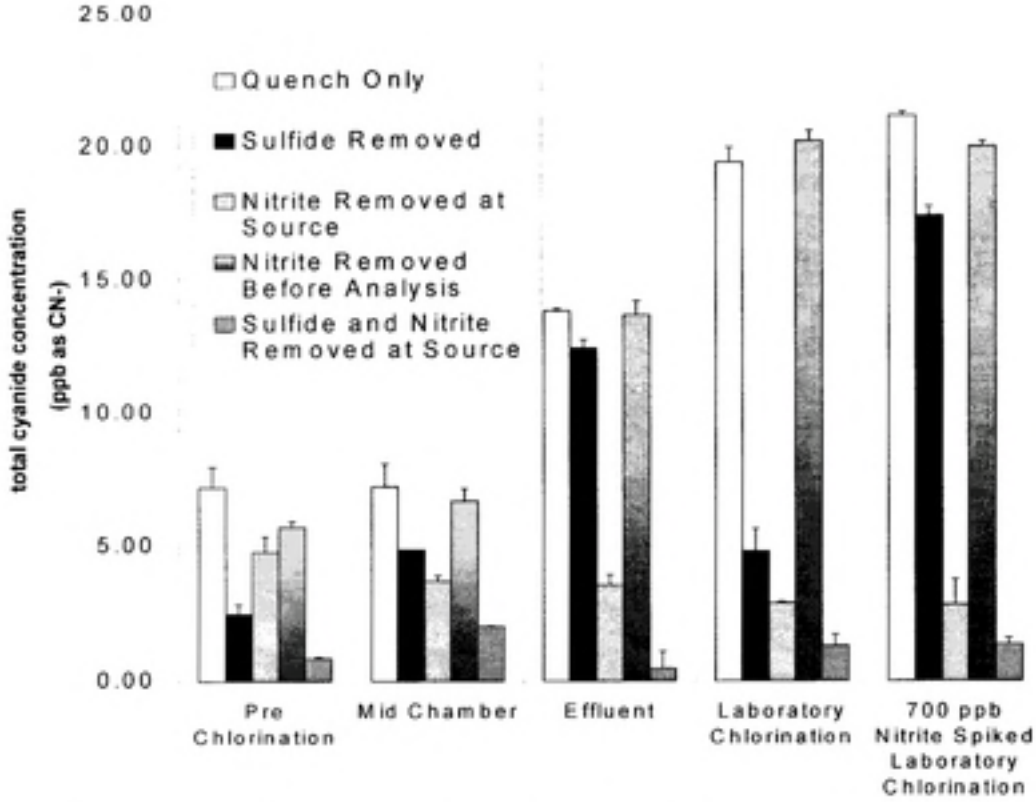

Figure 4.9 Total Cyanide Concentrations in the Muddy Creek Wastewater as a Function of Sample Collection Point and Stabilization Procedure

Table 4.12 Total Cyanide Concentrations for the Muddy Creek Wastewater Treatment Plant Samples as a Function of Sample Collection Point and Stabilization Procedure

	Total Cyanide Concentration (ppb as CN^-)	+/- (ppb as CN^-)
Quench Only		
Pre Chlorination	7.20	0.77
Mid Chamber	7.23	0.86
Effluent	13.80	0.08
Laboratory Chlorination	19.34	0.54
700 ppb Nitrite Spiked Laboratory Chlorination	21.05	0.14
Sulfide Removed		
Pre Chlorination	2.45	0.36
Mid Chamber	4.85	NA
Effluent	12.43	0.32
Laboratory Chlorination	4.77	0.84
700 ppb Nitrite Spiked Laboratory Chlorination	17.30	0.36
Nitrite Removed at Source		
Pre Chlorination	4.77	0.57
Mid Chamber	3.68	0.21
Effluent	3.52	0.38
Laboratory Chlorination	2.85	0.05
700 ppb Nitrite Spiked Laboratory Chlorination	2.79	0.94
Nitrite Removed Before Analysis		
Pre Chlorination	5.70	0.20
Mid Chamber	6.66	0.48
Effluent	13.65	0.53
Laboratory Chlorination	20.11	0.37
700 ppb Nitrite Spiked Laboratory Chlorination	19.90	0.19
Sulfide and Nitrite Removed at Source		
Pre Chlorination	bdl	0.04
Mid Chamber	bdl	0.02
Effluent	bdl	0.62
Laboratory Chlorination	bdl	0.41
700 ppb Nitrite Spiked Laboratory Chlorination	bdl	0.23

The pre-chlorination and the chlorine contact chamber samples that were only quenched have approximately the same cyanide level (7.2 ppb) while the effluent has a greater cyanide

concentration of 13.80 ppb. The same comparison done on the sulfide removed samples demonstrated the same increase in the effluent sample: ~3 ppb versus 12.43 ppb. The samples that had nitrite removed at source did not show this increase. These samples had a relatively constant cyanide concentration throughout the disinfection process (~4 ppb). The samples that were stabilized by nitrite removal just prior to analysis had the highest cyanide concentrations in the effluent sample (13.65 ppb).

These observations indicate that there was nitrite formation occurring between the chlorine contact chamber sample point and the effluent sample point. The nitrite caused some cyanide formation to occur in the sample vial that did not have any reagent to remove the nitrite interference. The samples that had the nitrite removed at the time of collection were unaffected by this additional nitrite since it was immediately removed when sampled due to the presence of the sulfamic acid. This nitrite interfered with the cyanide analysis for every stabilization procedure that does not remove nitrite at source.

The removal of sulfide lowered the cyanide concentration at every sample collection point and each laboratory chlorination. This can then be attributed to the removal of the sulfide interference in the sample. The flow injection analysis has proprietary reagents that claims to remove the sulfide interference up to a certain point. These reagents are clearly inadequate for sulfide removal as demonstrated by these results and indicates the continued need to precipitate and filter sulfide prior to analysis. More experimentation is required to inspect if any complexed cyanide associated with the suspended particles is removed during the filtration process in the sulfide removal stabilization procedure.

The removal of nitrite at source lowered the cyanide concentration at every sample collection point and each laboratory chlorination. The removal of nitrite at source prevented the proposed cyanide formation reaction from occurring in the sample vial while being held for analysis. This is further evidence for the proposed cyanide formation reaction.

The removal of nitrite was also done immediately before analysis to test whether this cyanide formation reaction was occurring in the sample vial or in the digester in the analytical method. Comparison of the nitrite removed at source samples to the nitrite removed before analysis samples can reveal when this cyanide formation reaction is occurring. The reason is that the only difference in these sample is the time when the sulfamic acid was added to the sample vials.

Analysis further reveals that the samples that had nitrite removed immediately before analysis had much greater cyanide concentrations than the nitrite removed at source samples. This is a clear indication that the cyanide formation reaction is occurring in the sample vial while being held for analysis. More proof of this hypothesis is shown when the nitrite removed immediately before analysis sample have cyanide concentration consistent with the quench only samples. This is indeed the case with these samples. The difference between the quench only samples and the nitrite removed before analysis samples are not statistically different.

The concurrent removal of sulfide and nitrite had the lowest cyanide concentrations (<2 ppb) when compared to the other stabilization procedures. It should be stressed that the nitrite removal component of this procedure was done at the time of sample collection. In fact, every concentration for this stabilization procedure is below the practical quantitation limit of the methodology (2 ppb). This stabilization procedure is the removal of both the nitrite and sulfide interference, so the fact that these concentrations are lower is due to the removal of these positive interferences with analysis.

The laboratory chlorination had higher cyanide concentrations than the other sample point for the quench only (19.34 ppb) and nitrite removed before analysis (20.11 ppb) stabilization procedures. The removal of nitrite at source lowers the cyanide concentration to be consistent with the effluent sample. This indicates that there was some nitrite formation in the wastewater sample before the chlorination experiment could be performed.

The same laboratory chlorination experiment was performed on a wastewater sample spiked with 700 ppb of nitrite. The rationale of this experiment was that a wastewater sample with a higher nitrite concentration might respond with a higher cyanide formation if chlorinated and an excess of the cyanide precursor material present in the wastewater. Results of this experiment were inconclusive. The cyanide concentration in the nitrite spiked sample when only quenched was greater by only 2 ppb. The cyanide concentration for the sulfide removed sample for the laboratory chlorination (4.77 ppb) was much lower than the sulfide removed, nitrite spiked laboratory chlorination (17.30 ppb). Nevertheless, this concentration is likely to be accurate since the nitrite removed before analysis sample (20.11 ppb) has the same concentration as the quench only laboratory chlorination (19.34). Explanation of the unrealistically low cyanide concentrations for the sulfide removed laboratory chlorination remains elusive.

4.10.2.2 Total Cyanide Results for Archie Elledge

Analysis of the Archie Elledge pre-chlorination wastewater revealed an extremely high nitrite concentration (3.13 mg/l). This is the greatest nitrite concentration seen of all the wastewater samples analyzed in this project. It would be anticipated that the cyanide concentrations in the chlorinated wastewater would be high due to the presence of the nitrite. Figure 4.10 and Table 4.13 summarize of the total cyanide concentrations for Archie Elledge.

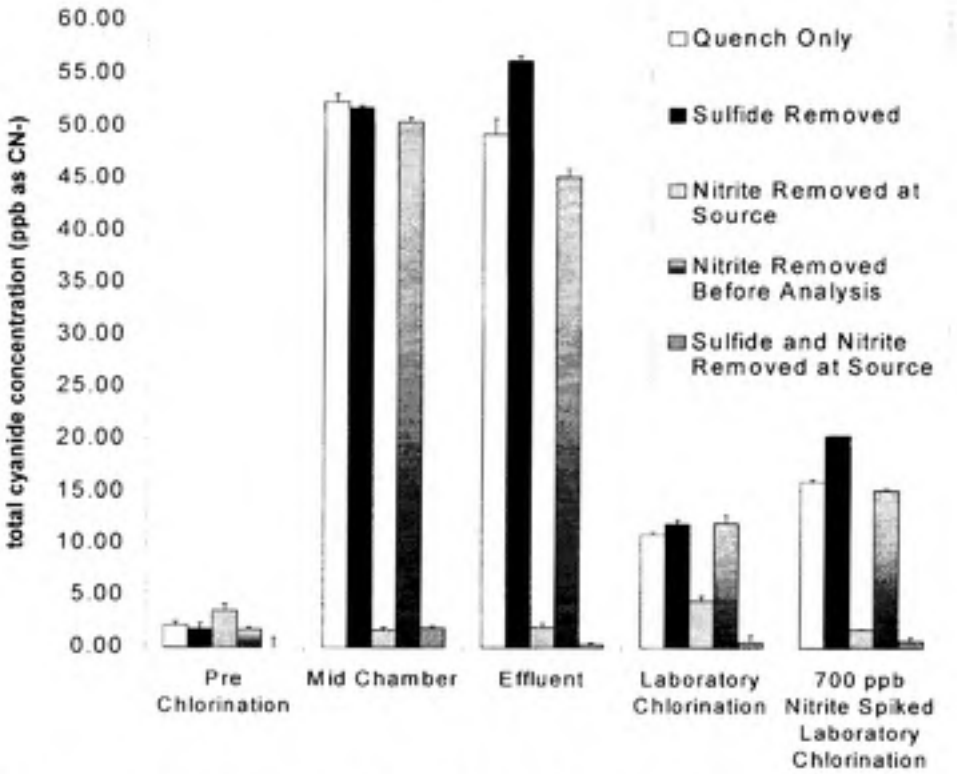

Figure 4.10 Total Cyanide Concentrations for the Archie Elledge Wastewater Samples as a Function of Sample Collection Point and Stabilization Procedure

Table 4.13 Total Cyanide Concentrations for the Archie Elledge Wastewater Samples as a Function of Sample Collection Point and Stabilization Procedure

	Total Cyanide Concentration (ppb as CN^-)	+/- (ppb as CN^-)
Quench Only		
Pre Chlorination	2.12	0.32
Mid Chamber	52.26	0.75
Effluent	49.14	1.52
Laboratory Chlorination	10.88	0.28
700 ppb Nitrite Spiked Laboratory Chlorination	15.96	0.18
Sulfide Removed		
Pre Chlorination	1.75 bdl	0.58
Mid Chamber	51.69	0.21
Effluent	56.08	0.45
Laboratory Chlorination	11.91	0.37
700 ppb Nitrite Spiked Laboratory Chlorination	20.26	0.01
Nitrite Removed at Source		
Pre Chlorination	3.54	0.58
Mid Chamber	1.66 bdl	0.21
Effluent	1.89 bdl	0.45
Laboratory Chlorination	4.48	0.42
700 ppb Nitrite Spiked Laboratory Chlorination	1.75 bdl	0.03
Nitrite Removed Before Analysis		
Pre Chlorination	1.68 bdl	0.22
Mid Chamber	50.37	0.39
Effluent	45.05	0.76
Laboratory Chlorination	11.97	0.81
700 ppb Nitrite Spiked Laboratory Chlorination	15.13	0.12
Sulfide and Nitrite Removed at Source		
Pre Chlorination	0.00 bdl	0.96
Mid Chamber	1.82 bdl	0.23
Effluent	0.31 bdl	0.17
Laboratory Chlorination	0.56 bdl	0.61
700 ppb Nitrite Spiked Laboratory Chlorination	0.72 bdl	0.30

The most obvious trend seen in these samples was the extremely high cyanide concentrations (~50 ppb) in the chlorine contact chamber and the effluent samples for the quench only, sulfide removed, and nitrite removed before analysis stabilization procedures. This can be only attributed to the cyanide formation associated with chlorinated wastewater samples in contact with high nitrite concentrations. While previous analysis demonstrated that the correlation of high nitrite concentrations to cyanide formations is not completely one to one, this evidence indicates that the nitrite is a necessary component in the reaction. The pre-chlorination samples had a cyanide concentration close to the practical quantitation limit of this methodology (2 ppb) for all the stabilization procedures, thus, leading to the conclusion that the chlorination is necessary for the cyanide formation reaction to occur.

The chlorine contact chamber and effluent samples had a cyanide concentration over 50 ppb for the quench only, sulfide removed, and nitrite removed before analysis stabilization procedures. These excessive cyanide concentrations were not seen in the chlorine contact chamber and effluent samples that had the nitrite removed at source. In fact, the cyanide concentration remained constant throughout the disinfection process at 2 ppb for the samples that had nitrite removed at source.

The samples that had sulfide and nitrite removed concurrently had the lowest cyanide concentrations when compared to other stabilization procedures. These samples were analyzed to be below the practical detection limit of the methodology. These low cyanide concentrations are due to the removal of both the sulfide and nitrite interferences.

The pre-chlorination wastewater was chlorinated at the same dosage (5 mg/l) as employed at the treatment plant was dosing at the time of sample collection. To compare the effect of nitrite, a 700 ppb nitrite spike laboratory chlorination was performed. The laboratory chlorination followed the same trends as outlined for the chlorinated samples collected at the treatment plant. For example, the removal of nitrite at source lowered the cyanide concentration when compared to the cyanide concentration of the nitrite removed before analysis sample. The removal of nitrite before analysis did not significantly change the cyanide concentrations when compared to the quench only sample. The concurrent removal of both sulfide and nitrite had the lowest cyanide concentrations.

One trend that was not consistent at other plants was that the removal of sulfide elevated the cyanide concentrations when compared to the quench only samples for both the laboratory chlorination and the nitrite spiked laboratory chlorination. One possible explanation is that the filters were contaminated to cause the higher cyanide readings. However, these results indicate that sulfide is not a contributing source of positive bias in total cyanide measurements at this plant.

Analysis of the nitrite spiked laboratory chlorination sample revealed higher cyanide concentrations than the unspiked laboratory chlorination for the following stabilization procedures: quench only, sulfide removal, and nitrite removal immediately before analysis. This is consistent with the findings of previous samples and the hypothesis of the cyanide formation reaction. These stabilization procedures will not remove nitrite at the time of sample collection. The samples, which were collected after the chlorination point in the wastewater treatment plant, experienced significantly high cyanide concentration. This is consistent with the hypothesis that the chlorination process produced compounds that reacted with nitrite to form cyanide while being held for analysis.

When nitrite is removed at source either alone or concurrently with sulfide removal, the cyanide concentration was not greater in the nitrite spiked sample. Surprisingly, the cyanide concentration was slightly lower in the nitrite spiked laboratory chlorination sample (4.48 ppb) than in the unspiked laboratory chlorination (<2 ppb) when nitrite is removed at source, but this difference is insignificant.

4.11 High Point Sample Results (Round 2)

A second sampling trip was organized to the High Point utility. The Eastside and Westside plants were sampled on September 18, 1998. These plants use chlorination as the disinfection process, and both plants are required to nitrify the wastewater. The discharge permit for these plants is 10 ppb.

4.11.1 Analysis of Nitrite for the High Point Wastewater Treatment Plants (Round 2)

The pre-chlorination wastewater from the Eastside and Westside plant was analyzed for nitrite content by ion chromatography. In addition to having the suspended solids removed through filtration, the samples also had chloride removed though the use of the silver filters as described

in Chapter 3 to assist better characterization of the nitrite peak. All calibrants and samples were analyzed in duplicate.

The Westside plant had high nitrite concentrations (1.27 mg/l) while the Eastside plant had much lower nitrite concentrations (98.01 ppb). The Eastside plant's nitrite concentration is of the same magnitude as most of the other wastewater treatment plants that have a well running nitrifying process. The Westside plant's nitrite concentrations are higher than seen at most of the other plants samples. The nitrite concentration and the standard deviation are given below in Table 4.14 for the Eastside and Westside plant.

Table 4.14 Nitrite Concentrations for the Pre-chlorination Wastewater Samples for the High Point Utilities (Round 2)

Pre-chlorination Wastewater Samples:

	Average Nitrite Concentration (ppb)	STD (ppb)
High Point Eastside	98.01	2.38
High Point Westside	1256	22.51

50 ppb nitrite spikes of the wastewater were analyzed in duplicate. The nitrite spike was added to the wastewater matrix before the suspended solids and chloride were removed. The evaluated recoveries identified whether the use of a chloride and suspended solids removal steps had an impact on nitrite analysis. The spike recoveries were calculated. The spike recovery for the Eastside plant was 118.40%, which is well within the accepted standards of the laboratory. The Westside plant had a negative spike recovery (-71.08%). This indicates that the nitrite spiked wastewater samples had a lower nitrite concentration than the unspiked sample. The cause of this was the fact that one of the spiked samples tested to have a rather low nitrite concentrations. When averaged with the duplicate, the spike recovery was still below zero. If this sample were to be ignored, the spike recovery would be 40.97%. This is still outside the range of acceptable recoveries. Explanation of this low of a recovery remains unexplained, hence the result of >1 mg/l is unreliable. A summary of the spike recoveries is given below as Table 4.15.

Table 4.15 Spike Recoveries for the High Point Pre-chlorination Wastewater Samples for High Point Utility (Round 2)

50 ppb Nitrite Spike Pre-chlorination Samples:

	Average Nitrite Concentration (ppb)	% Recoveries (%)	STD (ppb)
High Point Eastside	157.21	118.40	4.92
High Point Westside	1220.89	-71.08	56.72

4.11.2 Total Cyanide Analysis for the High Point Utility (Round 2)

4.11.2.1 Total Cyanide Analysis for the Eastside High Point Utility (Round 2)

The Eastside plant had low nitrite concentration (98.01 ppb), so it is not expected that there should be significant cyanide formations attributed to high nitrite concentrations. Each sample was analyzed in triplicate for total cyanide according to the procedure outline in Chapter 3.

Wastewater samples from the Eastside plant were collected at three different sample points: pre-chlorination, mid chlorine contact chamber, and effluent. The Eastside utility collected an effluent sample concurrently to be analyzed according to Standard Methods 4500-CN for compliance of the cyanide discharge permit. The total cyanide concentration according to the Standard Methods 4500-CN method was tested to be below the detection limit of 5 ppb. A laboratory chlorination was performed by chlorinating at the UNC laboratories an aliquot of the pre-chlorination wastewater at the same dose that was being used at the plant at the time of collection.

Figure 4.11 and Table 4.16 illustrate the cyanide concentration as a function of sample collection point and stabilization procedure. There appears to be no statistical difference between any of the stabilization procedures at a single sample point. The pre-chlorination samples all have a cyanide concentration of ~10 ppb. The fact that there is not a significant difference indicates that the nitrite and sulfide were not interfering with analysis. If any sulfide or nitrite were to cause elevated cyanide concentration, at least one of the stabilization procedures would show a significant decrease in the cyanide concentration. The detected cyanide can be attributed to influent sources to the wastewater treatment plant.

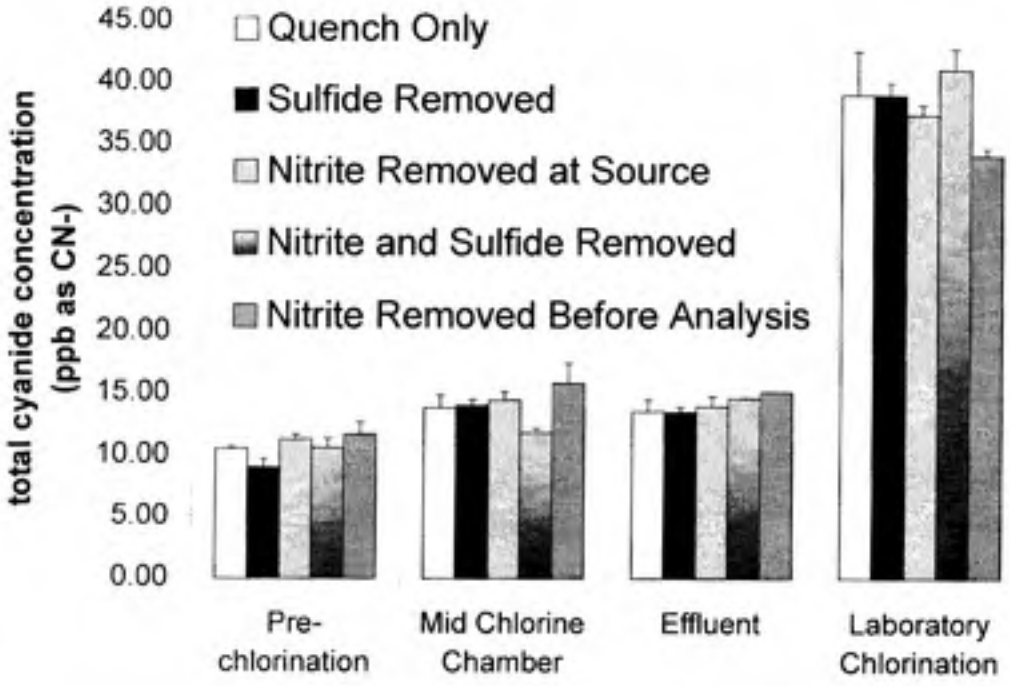

Figure 4.11 Total Cyanide Concentration for High Point Eastside (Round 2) as a Function of Sample Collection Point and Stabilization Procedure

Table 4.16 Total Cyanide Concentrations for High Point Eastside as a Function of Sample Collection Point and Stabilization Procedure

Wastewater Samples:

	Total Cyanide Concentration (ppb as CN-)	+/- (ppb as CN-)
Quench Only:		
Pre-chlorination	10.55	0.14
Mid Chlorine Chamber	13.79	1.06
Effluent	13.54	0.94
Laboratory Chlorination	38.99	3.52
Sulfide Removed:		
Pre-chlorination	9.06	0.64
Mid Chlorine Chamber	14.00	0.50
Effluent	13.45	0.47
Laboratory Chlorination	38.97	0.97
Nitrite Removed at Source		
Pre-chlorination	11.30	0.39
Mid Chlorine Chamber	14.44	0.73
Effluent	13.96	0.79
Laboratory Chlorination	37.37	0.78
Sulfide and Nitrite Removed		
Pre-chlorination	10.63	0.72
Mid Chlorine Chamber	11.86	0.35
Effluent	14.61	0.04
Laboratory Chlorination	41.04	1.66
Nitrite Removed before Analysis		
Pre-chlorination	11.72	0.95
Mid Chlorine Chamber	15.81	1.64
Effluent	15.12	NA
Laboratory Chlorination	34.00	0.62

The chlorine contact chamber samples had a slightly greater cyanide concentration of ~14 ppb. The cyanide concentration for the chlorine contact chamber samples remained constant no matter which stabilization procedure was employed. This indicates that the nitrite and sulfide

interferences were not present. The increase from the pre-chlorination samples to the mid chlorine contact chamber samples could be due to the heterogeneity of wastewater that lead to the difference in cyanide concentration.

The effluent samples had an average cyanide concentration (~14 ppb) that was not significantly different from the mid chlorine contact chamber samples. The cyanide concentration did not change depending on the stabilization procedure used. As with the other sample point, this indicates that the sulfide and nitrite were not interfering with analysis; thus, the detected cyanide is caused by cyanide influent to the chlorination process.

The laboratory chlorination, dosed at 5 mg/l, had much greater cyanide concentrations than the other sample points (>35 ppb), but there was not a significant difference between the stabilization procedures. Taking into account that the laboratory chlorination was performed on the sample a couple of days after the wastewater was collected, there must have been cyanide formation while the sample was being held for the laboratory chlorination to be done. The removal of nitrite should prevent the cyanide formation reaction from occurring. There is no statistical difference among the stabilization procedure used on the laboratory chlorination samples, so the cyanide must have been generated before these stabilization procedure were employed. Sulfide cannot be the cause of the elevated cyanide concentrations. If sulfide were to be generated in the sample, the stabilization procedures that remove sulfide would cause the cyanide concentration to be lower. Cyanide formation cannot be ruled out in the same manner. A sulfide solution will cause a positive response in the cyanide analyzer, but a pure nitrite solution will not cause a positive response. Nitrite is believed to be involved with a cyanide formation reaction. This reaction could have occurred in the sample before the chlorination and subsequent stabilization procedures were employed. This is the probable cause of the elevated cyanide concentrations in the laboratory chlorination.

The fact that there was not a significant cyanide formation in both the Eastside and the Westside plant indicate that there was either insufficient nitrite or cyanide forming carbon precursor material. The Westside plant had a high nitrite concentration while the Eastside had a moderate level. It is believed that these plants did not have the organic precursors to form cyanide. The same inspection of the first sampling trip to this utility reveals the same conclusion. These plants had a moderate nitrite concentration, but not a significantly large cyanide formation associated with the hypothesized two step cyanide formation reaction.

4.11.2.1.1 Evaluation of the Integrity of Total Cyanide in Various Stabilization Modes

To determine the impact of the stabilization procedures on cyanide in the wastewater matrix, 10 ppb total cyanide spikes were tested for each sample collection point and stabilization procedure. The wastewater was collected on site and was immediately spiked at ambient pH with 10 ppb total cyanide at the High Point Eastside wastewater treatment plant with a stock solution which comprised both free (48 mg/l) and complexed (54 mg/l) cyanide. The spiked wastewater was then stabilized as outlined in Chapter 3.

Table 4.17 outlines the results of this procedure. The spike recovery of the sample when compared to the unspiked sample keeping the stabilization procedure and sample collection point constant is also given in Table 4.15. 100% spike recovery was not expected since the wastewater was at ambient pH. The free cyanide component of the cyanide stock solution would have the chance to volatilize since it would be in the protonated form. The free cyanide comprises 47% of the total cyanide while the remaining complex component (53%) should remain in solution. The cyanide spike was added to the wastewater before the stabilization procedures were employed. This caused a chance for the cyanide to volatilize until the samples were capped to be head-space free. Because of this consideration, two separate spike recoveries were calculated. The first was based upon the total cyanide that was spiked to the wastewater sample, while the second was based on the amount of complexed cyanide added in that same cyanide spike.

Since the stabilization agents are added in excess to the sample vials, any spike recovery would indicate that the stabilization agent was not removing the cyanide from the sample. This is indeed the case. There is at least some spike recovery in each of the stabilization procedures. The samples that had nitrite removed before analysis had the lowest total cyanide spike recoveries (~30%). This is of concern since the Standard Method 4500-CN stabilization and preservation method is most similar to this method. There is no explanation of this lower recovery. The recoveries of the complex cyanide are greater than the total cyanide spike; however, the recoveries are low for some of the sample points indicating a loss of the complex cyanide. Since there was never a complete destruction of the complex component, it can be concluded that the stabilization procedures do not impact that total cyanide concentrations.

Table 4.17 Total Cyanide Concentration and Spike Recoveries for the 10 ppb total cyanide spiked High Point Eastside Wastewater Samples as a Function of Sample Collection Point and Stabilization Procedure

10 ppb TCN Spiked Samples:

	Total Cyanide Concentration (ppb as CN-)	Total Cyanide Concentration for the spiked solutions (ppb as CN-)	+/- (ppb as CN-)	% Recovery based on total cyanide added (%)	% Recovery based on complexed cyanide added (%)
Quench Only:					
Pre-chlorination	10.55	18.66	0.94	81.14	153.09
Mid Chlorine Chamber	13.79	18.77	0.13	49.83	94.02
Effluent	13.54	19.14	1.05	56.01	105.67
Sulfide Removed:					
Pre-chlorination	9.06	17.13	0.82	77.40	146.03
Mid Chlorine Chamber	14.00	20.35	0.88	45.00	84.90
Effluent	13.45	17.60	0.10	34.88	65.81
Nitrite Removed at Source					
Pre-chlorination	11.30	17.47	0.12	61.69	116.40
Mid Chlorine Chamber	14.44	19.58	0.26	51.36	96.91
Effluent	13.96	18.67	0.22	47.16	88.98
Sulfide and Nitrite Removed					
Pre-chlorination	10.63	16.80	1.50	61.68	116.38
Mid Chlorine Chamber	11.86	18.50	0.58	66.40	125.29
Effluent	14.61	16.94	0.12	23.30	43.96
Nitrite Removed before Analysis					
Pre-chlorination	11.72	15.04	0.90	33.28	62.79
Mid Chlorine Chamber	15.81	18.96	0.37	31.47	59.38
Effluent	15.12	18.45	0.09	33.23	62.71

4.11.2.2 Total Cyanide Results for High Point Westside (Round 2)

Analysis for nitrite concentration revealed a high concentration measured at 1.26 mg/l. A high cyanide concentration would be expected if both a high nitrite concentration and cyanide forming precursor materials are both present.

The total cyanide concentration in the effluent sample collected by the utility and analyzed by the contract laboratory according to the Standard Methods 4500-CN method was tested to be below the detection limit of 5 ppb. A laboratory chlorination was performed by chlorinating, at the UNC laboratories, an aliquot of the pre-chlorination wastewater at the same dose that was being used at the plant at the time of collection (5 mg/l).

Figure 4.12 and Table 4.18 illustrate the cyanide concentration as a function of sample collection point and stabilization procedure. The quench only stabilization procedure had the greatest cyanide concentration when compared to the other sample stabilization procedures for all samples collected at the treatment plant. For the laboratory chlorination, the quench only sample as the lowest compared to the other stabilization procedures. There appears to be no other trend between the stabilization procedures.

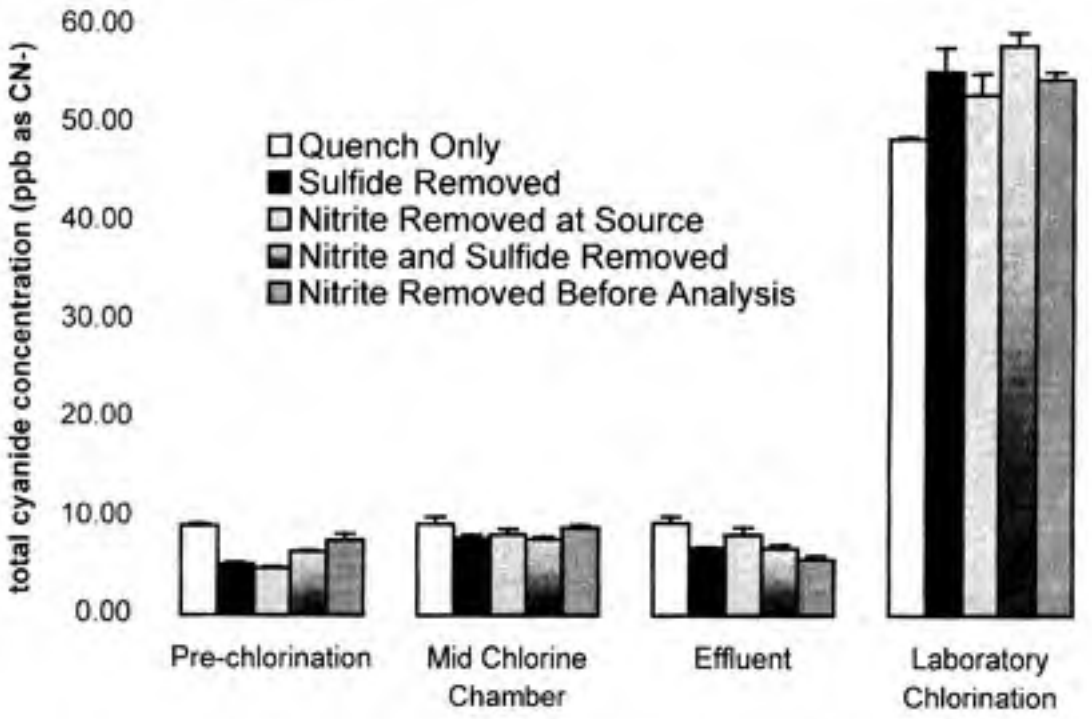

Figure 4.12 Total Cyanide Concentration for the High Point Westside (Round 2) Wastewater Samples as a Function of Sample Collection Procedure and Sample Collection Point

Table 4.18 Total Cyanide Concentrations for the High Point Westside Utilities as a Function of Sample Stabilization Procedure and Sample Collection Point

Wastewater Samples:

	Total Cyanide Concentration (ppb as CN-)	+/- (ppb as CN-)
Quench Only:		
Pre-chlorination	9.09	0.19
Mid Chlorine Chamber	9.22	0.74
Effluent	9.34	0.67
Laboratory Chlorination	48.35	0.23
Sulfide Removed:		
Pre-chlorination	5.24	0.10
Mid Chlorine Chamber	7.81	0.37
Effluent	6.84	0.08
Laboratory Chlorination	55.22	2.45
Nitrite Removed at Source		
Pre-chlorination	4.78	0.13
Mid Chlorine Chamber	8.21	0.49
Effluent	8.18	0.75
Laboratory Chlorination	52.92	2.04
Sulfide and Nitrite Removed		
Pre-chlorination	6.43	0.13
Mid Chlorine Chamber	7.75	0.25
Effluent	6.79	0.40
Laboratory Chlorination	57.91	1.29
Nitrite Removed before Analysis		
Pre-chlorination	7.60	0.69
Mid Chlorine Chamber	8.86	0.27
Effluent	5.66	0.34
Laboratory Chlorination	54.44	0.77

The chlorine contact chamber samples had a slightly greater cyanide concentration of ~8 ppb when compared to the pre-chlorination samples (~6 ppb). The cyanide concentration for the

chlorine contact chamber samples remained constant no matter which stabilization procedure was employed. This indicates that the nitrite and sulfide interferences were not present. The increase from the pre-chlorination samples to the mid chlorine contact chamber samples could be due to the heterogeneity of wastewater that lead to the difference in cyanide concentration.

The effluent samples had an average cyanide concentration (~7 ppb) that was not significantly different from the mid chlorine contact chamber samples. The cyanide concentration did not change depending on the stabilization procedure used. As with the other sample point, this indicates that the sulfide and nitrite were not interfering with analysis; thus, the detected cyanide is caused by cyanide influent to the chlorination process.

The laboratory chlorination had much greater cyanide concentrations than the other sample points (>45 ppb). Like the other sample points, there is not a significant difference between the stabilization procedures. Although the quench only sample has the lowest cyanide concentration, the error of analysis makes this insignificant. Taking into account that the laboratory chlorination was performed on the sample a couple of days after the wastewater was collected, there must have been cyanide formation while the sample was being held for the laboratory chlorination to be done. Sulfide cannot be the cause of the elevated cyanide concentrations. If sulfide were to be generated in the sample, the stabilization procedures that remove sulfide would cause the cyanide concentration to be lower. Cyanide formation cannot be ruled out in the same manner. The presence of sulfide will cause a positive response in the cyanide analyzer, but a nitrite will not. Additional nitrite, which may have been generated in situ due to partial nitrification, could engage a particular carbon source in the wastewater to generate condition appropiate to cyanide formation during chlorination. Since the nitrite was only removed after chlorination, these results serve to indicate a process different from that obtained in the treatment plant samples. This reaction could have occurred in the sample before the chlorination and subsequent stabilization procedures were employed. This is the probable cause of the elevated cyanide concentrations in the laboratory chlorination.

4.12 Summary of the Impact of Nitrite on Cyanide Concentrations During Wastewater Chlorination

It was observed at many plants that the removal of nitrite at the time of sample collection decreased the levels of total cyanide. The hypothesis was that the nitrite reacted with a carbon precursor generated during chlorination to form cyanide in the sample vial while being held for

analysis. Table 4.20 summarizes the cyanide concentration for samples that were collected in the chlorine contact chamber and which were stabilized by either only quenching or by both quenching and removing nitrite. The samples that had nitrite removed at source and just before analysis are also specified. The associated nitrite levels in the pre-chlorinated wastewater is also given. The general observation is that the higher nitrite concentrations contributed to significant cyanide formation in the mid chlorine contact chamber samples. High Point Westside (Round 2) and North Buffalo are notable exceptions to this trend. For these plants, there was a relatively high nitrite concentration, but with no extreme cyanide formation in the mid chlorine contact quench only sample. It is believed that these samples did not have the reactive carbon compounds formed in the chlorination process that are concurrently needed with nitrite to form cyanide.

The removal of nitrite just prior to analysis dramatically affected the total cyanide concentration when compared to samples that had the nitrite removed at the time of sample collection. The removal at source decreased the total cyanide levels in all but three samples. The samples in which the total cyanide concentration was not decreased did not experience a dramatic cyanide formation as with other samples. The lack of the cyanide formation could be due to the lack of nitrite or organic precursors. There is also a strong correlation between the quench only samples and the samples that had nitrite removed just prior to analysis. This is a further indication that the cyanide formation is occurring before the sample is being analyzed.

Table 4.19 A Summary of the Impact of Nitrite on Cyanide Levels for the Wastewater Treatment Plants Surveyed in the Project

		Cyanide Concentration in Mid Chlorine Contact Chamber		
Sample Site	Nitrite Concentration	Quenched Only	Nitrite Removed at Source	Nitrite Removed Just Prior to Analysis
	(ppb)	(ppb as CN-)	(ppb as CN-)	(ppb as CN-)
South Burlington	736	43.3	6.14	NA
East Burlington	84.4	2.56	3.11	NA
High Point Eastside	68.1	7.27	2.36	7.28
High Point Westside	76.2	7.51	5.18	5.9
T.K. Osborne (Greensboro)	66.4	11	10.6	NA
North Buffalo (Greensboro)	2310	7.45	9.16	NA
Muddy Creek (Winston-Salem)	bdl	7.23	3.68	6.66
Archie Elledge (Winston-Salem)	3130	52.3	bdl	50.37
High Point Eastside (Round 2)	98	13.8	14.4	15.81
High Point Westside (Round 2)	1260	9.22	8.21	8.86

bdl - below detection limit
NA - not available

CHAPTER 5

CONCLUSIONS AND RESEARCH NEEDS

5.1 CONCLUSIONS

This study investigated the levels of total cyanide in wastewater treatment plants practicing chlorination and in particular the possible formation of cyanide during subsequent sample handling. Wastewater samples collected at eight different wastewater treatment plants allowed for the study of this cyanide formation. Since the wastewater samples varied between plants and sampling events, a variety of chemical constituents were monitored for their impact including sulfide, nitrite, and free chlorine. Optimization of a flow injection procedure for rapid and accurate measurements of total cyanide was carried out to achieve the goals of this project. The conclusions from this study are as follows:

1. The removal of free chlorine (quenching) should be done with meta-arsenite. Other approved agents such as ascorbic acid and thiosulfate will interfere with the cyanide analysis. The former has been shown to be involved with a cyanide formation reaction with nitrite, while the latter may be a source of sulfide following degradation in the UV digestion chamber in the flow injection procedure.

2. Sulfide removal (if present) will lower the apparent cyanide concentration by an amount proportional to its concentration in wastewater. Sulfide is a direct positive interference with the flow injection method of total cyanide analysis. The removal, through chemical precipitation with a heavy metal, is necessary, as demonstrated by this research, even though flow injection analysis reagents include a constituent to precipitate the sulfide and remove it from the sample.

3. Wastewater with high nitrite concentration generated elevated cyanide levels during sample processing when chlorinated and when the nitrite was not removed at the time of sample collection.

4. Removal of nitrite just before analysis, as suggested by Standard Method 4500-CN, does not remove the nitrite interference for cyanide analysis. The cyanide concentration for the samples that had nitrite removed only before analysis correlated very well with the wastewater samples that were only quenched and in which nitrite appeared to generate total cyanide during sample holding.

5. Cyanide formation may occur in the sample vial while being held for analysis and not in the distillation step of the Standard Method 4500-CN. Comparison of the samples that had nitrite removed at the time of sample collection with samples that had nitrite removed immediately prior to analysis reveal that the nitrite must be removed at the time of sample collection. In most plant wastewaters, there is a large difference in the cyanide concentration for these samples. The only difference between these samples is the length of time that the samples were in contact with the nitrite.

6. The cyanide formation reaction appears to be a two step reaction. The first step of the reaction occurs in the chlorine contact chamber when a constituent reactive carbon reacts with chlorine to form another second compound which then reacts with nitrite in the sample vial to form cyanide.

7. Standard Method 4500-CN should be modified to require nitrite removal at the time of sample collection, and to discourage the use of thiosulfate and ascorbic acid as chlorine quenching agents.

5.2 Research Needs

The following are necessary for further research in the field of cyanide formation associated with nitrite and chlorine:

1. A more complete understanding of the role nitrite plays in the cyanide formation. A high nitrite concentration does not always result in cyanide formation. Other chemical species must be involved to limit this reaction. Even low nitrite concentrations have been demonstrated to cause some cyanide formation, and high nitrite concentration often caused excessive amount of cyanide formations.

2. More study is needed to test if the removal of sulfide also removed cyanide associated with the suspended material in the wastewater samples. The sulfide is removed through filtration of the chemically precipitated form. The dominant form of cyanide is the iron complex, so removal through filtration of the complexed cyanide is possible.

3. Identification of the carbon groups that react with nitrite and the intermediates that react with chlorine generating cyanide could possibly move the burden from the municipal wastewater treatment plants to the industrial wastewater treatment plants generating the precursor material.

REFERENCES

APHA (1995). Standard Methods for the Examination of Water and Wastewater. 19th Edition. APHA, AWWA, WEF, Washington, DC.

Billard, J. and P. Roubaud (1985). The Effect of Metals and Cyanide on Fertilization in Rainbow Trout (*Salmo gairdneri*). Water Research, 10: 813-814.

Blaha, J. (1976). Mathematical Analysis of the Chemical System 'Cyanide-Heavy Metals' in Water – Determination of Components and Toxicity of the System – I. The Theoretical Solution. Water Research, 10:815-819.

Carr, S. A., R. B. Baird and B. T. Lin (1994). Wastewater Derived Interferences in Cyanide Analysis. Water Research, 31:7:1543.

CRC (1995). CRC Handbook of Chemistry and Physics. 76th Edition, David R. Lide (ed.), CRC Press, Boca Raton.

Cotton, F. A., and G. Wilkinson (1972). Advanced Inorganic Chemistry: A Comprehensive Text. Wiley-Interscience, New York.

Doudoroff, P. (1976). Toxicity to Fish of Cyanides and Related Compounds. EPA 600/3-76-038, U.S. Environmental Protection Agency, Diluth, Minnesota.

Ganczarczyk, J. J., P. T. Takoaka and D. A. Ohashi (1985). Application of Polysulfide for Pretreatment of Spent Cyanide Liquors. Journal of Water Pollution Control Federation, 57:1089-1093.

Kenfield, C. F., R. Qin, M. J. Semmens and E. L. Cussler (1988). Cyanide Recovery Across Hollow Fibre Gas Membranes. Environmental Science and Technology, 22: 1151-1155.

Lester, J. N. (1990). The Treatment of Toxic Wastes. In: R.M. Harrison (Ed.), Pollution: Causes, Effects and Controls. Royal Society of Chemistry, Cambridge, UK.

Lordi, D. T., C. Lue-Hing, S. W. Whitebloom, N. Kelada and S. Dennison (1980). Cyanide Problems in Municipal Wastewater Treatment Plants. Journal of Water Pollution Control Federation, 52:3:597.

Meeussen, J. C. L., M. G. Keizer and F. A. M. de Haan (1992). Chemical Stability and Decomposition Rate of Iron Cyanide Complexes in Soil Solutions. Environmental Science and Technology, 13: 1481-1487.

Metcalf and Eddy Inc. (1991). Wastewater Engineering. Treatment, Disposal, and Reuse. McGraw Hill, New York, 3rd Edition.

Pohlandt, C., E. A. Jones and A. F. Lee (1983). A Critical Evaluation of the Methods Applicable to the Determination of Cyanides. Journal of the South African Institute of Mines and Metals, 83: 11-19.

Rapean, J. C., R. A. Johnson and T. P. Hanson (1980). Biodegradation of Cyanide: Nitrite Interference in the Standard Test for Total Cyanide. Proceeding of the 35th Annual Industrial Waste Conference, Perdue University, Lafayette, Indiana.

Reynolds, T. D. and P. A. Richards (1996). Unit Operations and Processes in Environmental Engineering. Second Edition, PWS Publishing Company, Boston.

Sekerka, I. And J. F. Lechner (1976). Potentiometric Determination of Low Levels of Simple and Total Cyanides. Water Research, 10:497-483.

Theis, T. L. and M. J. West (1986). Effects of Cyanide Complexation on Adsorption of Trace Metals at the Surface of Geothite. Environmental Technology Letters, 7: 309-318.

USEPA (1978). Total Cyanide (Colormetric, Automated UV). EPA Method 335.3, Environmental Protection Agency, Diluth, Minnesota.

USEPA (1984). Ambient Water Quality Criteria for Cyanide. EPA 440/5-84-028, Environmental Protection Agency, Diluth, Minnesota.

Weber, W. J. Jr. and F. A. DiGiano (1996). Process Dynamics in Environmental Systems. John Wiley and Sons, Inc., New York, New York.

Wild, S. R., T. Rudd and A. Neller (1994). Fate and Effects of Cyanide During Wastewater Treatment Processes. The Science of the Total Environment, 156:2:93.

Woods C. W. and A. K. Holliday (1967). Inorganic Chemistry. 3rd Ed., Butterworths Press, London.

WHO. (1988). Guidelines for Drinking Water Quality Vol. 2. Health Criteria and Other Supporting Information. Geneva.

Yoshida, T., Y. Tamaura and T. Katsura (1983). Practical Method for Determination of Total Cyanide in Metal-Containing Wastewaters. Environmental Science and Technology, 17:439-441.

Young, T. C. and T. L. Theis (1991). Determination of Cyanide in Manufactured Gas Plant Purifier Wastes. Environmental Technology Letters, 12: 1063-1069.

APPENDIX A

SAMPLE STABILIZATION METHOD FOR ONE LITER SAMPLE COLLECTION VOLUME

Sample Stabilization and Preservation for Cyanide Analysis

Chemicals Needed:

1. Sodium meta-Arsenite ($NaAsO_2$) solid
2. Sulfamic Acid (H_2NSO_3H) solid
3. Lead Carbonate ($PbCO_3$) solid
4. Sodium Hydroxide (NaOH) 50% w/w solution
5. Deionized Water (DIW)

Solution Preparation:

11.3 g/l Sodium meta-Arsenite as meta-arsenite:

- Place 1375 mg of sodium meta-arsenite made up to 100 ml with deionized water

12.7 g/l Sulfamic Acid

- Place 635 mg of sulfamic acid made up to 50 ml with deionized water

Sample Stabilization Procedure:

Four different stabilization procedures are employed with this methodology prior to raising the pH above 12. The first is to only quench the chlorine from the sample. The second stabilization procedure is to quench the chlorine and to remove sulfide from the sample. The third stabilization procedure is to quench the chlorine and to remove the nitrite from the sample. The final stabilization procedure is to remove both sulfide and nitrite and to quench the chlorine from the sample.

Chlorine Quenching Only:

1. Place 2 ml of the 11.3 g/l meta-arsenite solution into a clean, one liter, high density polypropylene bottle
2. Add the wastewater sample to the bottle such that there is no headspace
3. Cap and mix the contents of the bottle
4. Add 5 ml of 50% w/w sodium hydroxide to the sample bottle

5. Cap and mix the contents of the bottle

Chlorine Quenching and Removal of Sulfide:

1. Place 2 ml of the 11.3 g/l meta-arsenite solution and a small spatula full of lead carbonate (~ 150 mg) into a clean, one liter, high density polypropylene bottle
2. Add the wastewater sample to the bottle such that there is no headspace
3. Cap and mix the contents of the bottle
4. Filter through a 0.45 μm nylon filter using a vacuum filtration device into a clean, one liter, high density polypropylene bottle
5. Add 5 ml of 50% w/w NaOH to the filtered sample
6. Cap and mix the contents of the bottle

Chlorine Quenching and Removal of Nitrite:

1. Place 2 ml of the 11.3 g/l meta-arsenite solution and 1 ml of the 12.7 g/l sulfamic acid solution into a clean, one liter, high density polypropylene bottle
2. Add the wastewater sample to the bottle such that there is no headspace
3. Cap and mix the contents of the bottle
4. Add 5 ml of 50% w/w sodium hydroxide to the sample bottle
5. Cap and mix the contents of the bottle

Chlorine Quenching, Removal of Sulfide, and Removal of Nitrite:

1. Place 2 ml of the 11.3 g/l meta-arsenite solution, a small spatula full of lead carbonate (~ 150 mg), and 1 ml of the 12.7 g/l sulfamic acid solution into a clean, one liter, high density polypropylene bottle
2. Add the wastewater sample to the bottle such that there is no headspace
3. Cap and mix the contents of the bottle
4. Filter the sample with a 0.45 μm nylon filter using a vacuum filtration device into a clean, one liter, high density polypropylene bottle
5. Add 5 ml of 50% w/w NaOH to the filtered sample
6. Cap and mix the contents of the bottle

Please note that this is the method that is employed for use of the flow injection analysis for cyanide. There may be changes to this method for the Standard Method for cyanide analysis to be feasible i.e. required sample volume. If the necessary equipment is not available to complete

this procedure, contact Steven Cook or Dr. Howard Weinberg to get suppliers addresses and phone numbers (Steven.Cook@sph.unc.edu or (919) 966-3859). Please avoid using plastic bottles or pipettors because of possible contamination issue; however, high-density polypropylene is not a problem.